

Pozzolanic Characteristics of Local Kaolin for Use in Blended Cements

El-Sharif M. Ibrahiem¹, Alyamani. A. Arabi¹, Mohamed S. B. Ahmed³

^{1*}Department of Civil Engineering, Faculty of Engineering Science, University of Nyala – Sudan,

²Department of Civil Engineering, Faculty of Engineering Science, Alzaiem Alazhari University - Sudan

Corresponding Author: El-Sharif M. Ibrahiem

Abstract: -

In this study, the potential use of a local kaolin in the manufacturing of blended cements was investigated, the material was characterized for its chemical, physical, mineralogical, and thermal properties using various techniques such as X-Ray Fluorescence (XRF), First derivative of Thermogravimetry (DTG), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD). Then the produced Metakalin (MK) was used to prepare blended cement for subsequent testing, different substitution levels of 10, 20, 30, and 40% of metakaolin were used with an Ordinary Portland cement OPC. The chemical, physical, and mineralogical analysis of sample showed its congruent with other kaolin found, and in use as supplementary cementitious materials, around the world. The results showed that the local kaolin has composition with a $SiO_2+Al_2O_3+Fe_2O_3$ content of 79.96%. The physical analysis results including Standard consistencies and setting times showed an increase in water demand with increasing substitution level. The strength activity index was found to be 102%, against 80% required by ASTM C-618 and IS:1344, respectively. Further tests revealed that when the ground MK replaced 10, 20, 30, and 40% w/w of OPC, the blended cements produced had a compressive strengths 42, 42, 37, 36 MPa respectively against 41 MPa for control mix at 28 days curing period. These findings suggest that this material is of high reactivity and can be used in the production of blended cements.

Keywords: Kaolin, Blended Cement, Physical Properties, Compressive Strength, Pozzolanic Reactivity

Date of Submission: 20-07-2021

Date of Acceptance: 04-08-2021

I. Introduction

Pozzolanic materials are widely used as supplementary cementitious materials in Portland cements to replace a part of clinker in order to enhance the performance of cement hydration. Such composite or blended cements are employed for their economical, ecological, and technological benefits. Also to reduce the energy consumption as well as CO₂ emission. Supplementary cementing materials reduce lime content in hydrated Portland cements and replace it with pore-filling cement hydrates, which are known to improve the ultimate strength, impermeability and durability to chemical attack of cement [1]. Blended cements (Portland Pozzolona Cement) can generally be used wherever OPC is usable under normal conditions. It is particularly useful in marine and hydraulic structures and large mass concrete structures.

Pozzolanas are defined as siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious values but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties, [2], [3]. The pozzolanas classified into Natural and Artificial; the Natural Pozzolans (NP) are products of volcanogenic activities such as volcanic ash, volcanic tuff, pumice, shales and diatomaceous. Natural pozzolanas requiring no energy inputs prior to utilisation. [3], [4], while the Artificial Pozzolanas are residues of waste industrial and agricultural products such as fly ash and rice husk.

Definition of pozzolanic reaction is the chemically reaction between a pozzolana (S) and calcium hydroxide (CH) in the presence of water (H). It can be generalized by the simplified equation shown in Equation(1),[5].



There are many benefits of using pozzolanic materials in cement and concrete amongst them are:

- 1/ Their ability to convert calcium hydroxide to calcium silicate hydrate (C-S-H), therefore, the capillary voids are either eliminated or reduced in size. This in turn improves cement-concrete material such as strength and durability of the hydrated paste.
- 2/ Pozzolans can also be used as cement replacement material (it is also economical since most pozzolanas are cheaper than cement they are replaced).

Metakaolin is produced by controlled calcinations of kaolin clay. The calcinations process drives off water from the kaolinite mineral ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), and resulting in an amorphous aluminosilicate ($Al_2O_3 \cdot 2SiO_2$), metakaolinite. This process is known as dehydroxylation, [6], and presented by simple equation: $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \uparrow$ (2)

The main objective of this study was to determine the pozzolanic activity of local kaolin by considering: (a) the influence of chemical and mineral composition on the reactivity; (b) the effect of thermal transformation of kaolinite on the production of amorphous silica.

The thermal transformation of kaolinite clay is affected by the heating parameters such as temperature, heating rate, and time, as well as cooling, which is significantly influence the dehydroxylation process, [6-12]. The major quantitative criterion for evaluating the performance of kaolinite by thermal treatment is a degree of the dehydroxylation, (Dtg):

$$Dtg = (M/M_{max}) \dots\dots\dots(3)$$

where M and Mmax are residual and maximum sample mass loss, respectively. For pure kaolinite (39.5% Al_2O_3 , 46.5% SiO_2 and 14% H_2O). The dehydroxylation in ambient atmosphere results in mass loss of about 14% and Dtg = 1, [13 – 14], which corresponds to mass in bound hydroxyl ions in kaolinite. The optimum calcining temperature to covert kaolin into metakaoline was studied using thermal analysis combined with thermal gravimetric analysis, (DSC-DTG) techniques, and XRD. The three regions of thermal analysis used in this study can be distinguished by: dehydroxylation region (Dtg < 0.9), metakaolinite region (0.9 < Dtg < 1), and spinel region (Dtg = 1) [15].

II. Materials And Methods

2.1. Materials

To reach the purposes of this research, an experimental laboratory study was developed using the following materials:

2.1.1. Cement and sand

Ordinary Portland cement (OPC) procured from Atbara cement company and river sand collected from Wadi Nyala, Sudan, were used in this study. The sand was washed, dried, and sieved into different fractions, it was standardized according to Indian Standard [16] to three grades; fine (90 µm to 500 µm), medium (500 µm-1mm), and coarse (smaller than 2mm-and greater than mm) fractions. Table 1 shows the chemical analysis results of Atbara cement and Wadi Nyala sand.

Table 1: Chemical properties of Atbara OPC and Wadi Nyala sand

Material	Chemical Composition (%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI
OPC	20.82	4.41	2.63	63.38	0.07	2.83	1.26	1.2	2.4
SAND	82.5	0.72	0.26	8.75	0.76	-	0.1	0.06	6.4

2.1.2. kaolin

A kaolin samples were collected from Saraf Omra area (latitude 13°29'31.61"N, and longitude 23°18'6.12"E), Sudan. kaolin was first studied for chemical composition. Metakaolin is produced by controlled calcinations of kaolin clay. Then, the representative sample was obtained by pulverized quartering process and grounded and sieved to grain size of less than 63 µm, and then characterized using chemical, physical, and x-ray diffraction analysis.

2.1.3. Water: Tap Water was used for the mixing and the curing of the mortar cubes.

2.2 Methods

2.2.1 Testing of pozzolanic reactivity

As a primary step in this study, the pozzolanic reactivity of MK with Portland cement was examined in the term of compressive strength following the procedures described in [17].

For the pozzolanic activity with OPC, a control mix was prepared in 50 mm cubes moulds. The control mix was produced using OPC as binder, while in other mix, MK: OPC: standard sand in proportion (1: 2N: 9) by weight were casted, cured, and tested at 7, and 28 days. where N is the ratio of specific gravity of pozzolana to specific gravity of cement. The details of mix proportions are shown in Table 2.

Table 2. Mix proportions for pozzolanic reactivity with OPC following [17]

Control Mix		Pozzolana-cement mix	
Component	Amount (g)	Component	Amount (g)
OPC	450	OPC	400
MK	0	MK	83
Standard sand	1350	Standard sand	1350
flow	105 ± 5	flow	105 ± 5

2.2.3 Preparation of blended cement mortar

A control mix was prepared in 70.7 mm cube moulds (area of face 50 cm²) composed of one part of cement, three parts of standard sand by mass, and (P/4 + 3.0) percent (of combined mass of cement and sand) water. Where P is the standard consistency, and prepared, stored and tested in the manner described in [18]. The ground MK was used to replace 10%, 20%, 30%, and 40% of the mass of OPC in the control mix. The compressive strengths of all mixes were measured at 7, 28, and 90 days. The details of mix proportions are shown in Table 3.

Table 3: Mix Proportion for blended Mortar

Mortar code	Blending Ratio (by weight %) (B)		Binder to aggregate (B:AG) by weight	No of Specimens	Test age Day
	OPC	MK			
MCTR	100	-	1:3	9	7, 28, 90
MMk10	90	10	1:3	9	7, 28, 90
MMk20	80	20	1:3	9	7, 28, 90
MMk 30	70	30	1:3	9	7, 28, 90
MMk 40	60	40	1:3	9	7, 28, 90

III. Results And Discussions

3.1 Chemical properties

The chemical analysis results of metakaolin presented in Table 4. The results indicated that the principal oxides of Silica (SiO₂), Alumina (Al₂O₃) and Iron (Fe₂O₃) were substantially present in the samples investigated with the sum oxides of 79.92. The analyses also showed the presence of minor element, while the loss on ignition (LOI) of the sample evaluated was 15.3%. These results are within the limitations of [19] and [2].

Table 4: Mix Proportion for blended Mortar

Material	Chemical Composition (%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	LOI
MK	43.66	35.29	0.97	1.79	0.255	0.063	0.29	0.04	15.3

3.2 Physical properties of materials

The physical properties such as specific gravity and fineness (by sieving and specific surface area) of the cement and pozzolana, were determined according to [18]. The results presented in Table 5

Table 5. Physical Properties of OPC and MK

Material	Specific Gravity	Fineness measured			Fineness Requirements	
		Passing sieve No %		Blaine Surface area cm ² /g	[20]	[19]
		90 micron	45 micron		cm ² /g	cm ² /g
OPC	3.15	94	-	2650	2250	-
MK	2.6	100	87	7688		3250

3.3 Reactivity test results

The reactivity of MK toward lime and OPC is measured through the compressive strength of standard mortar tests according to [17]. The results of the MK reactivity with lime is 4.9 Mpa. at age of 8 days, [19], required a minimum of 4.0 MPa. While the compressive strength with OPC were, 40, and 42 MPa, at 7, and 28 days respectively, against 36.7 MPa, and 41.3 MPa for the reference mortar. The strength reactivity of MK at 28

days was obtained is 102%, however the minimum required by [19] is 80% of the strength corresponding reference mortar in case of pozzolana to be used for manufacture of Portland pozzolana cement.

3.4 Results of TG-DSC and XRD analysis of MK

Thermal behaviors of the raw MK are presented in Table 6, Figure 1, and 2. The main changes revealed by TG and DTG analysis showed that, the temperatures below about 200 °C releases the water absorbed in pores and at the surfaces. Between 200°C and 450 °C, the mass loss attributed to the pre-dehydration process takes place, as a result of the reorganization in the octahedral layer. In the temperature range 448–672 °C, dehydroxylation of kaolinite and formation of metakaolinite takes place, the observed endothermic peak with a maximum at 492 °C may be attributed to dehydroxylation process. The mass loss between temperatures of 400 - 600 °C was 12.1 Wt % . The maximum temperature is selected so that the specimen weight is stable at the end of the experiment (i.e., 751 °C).

Table 6 implying that all chemical reactions are completed (i.e., all of the carbon is burnt off leaving behind metal oxides). This approach provides two important numerical pieces of information the temperature of the maximum in the weight loss rate ($T_o = dm/dT_{max}$) and the weight loss onset temperature (T_{onset}). The former refers to the temperature of the maximum rate of oxidation, while the latter refers to the temperature when oxidation just begins.

Table 6: Thermal analysis data for kaolin

Temp. °C;	DSC	Mass loss %	DTG
21.48200	-6.8438e-002	100.0000	1.6667e-002
51.48200	-5.5856e-002	99.86666	-5.8293e-002
101.48200	-3.1669e-002	99.63333	-6.4350e-002
151.48200	4.2587e-003	99.26667	-6.5750e-002
153.98200	6.3136e-003	99.23358	-7.0402e-002
201.48200	4.5351e-002	98.79661	-7.6708e-002
251.48200	8.9003e-002	98.60000	-4.1674e-003
301.48200	0.12499	98.43334	-3.4755e-002
351.48200	0.14201	98.03254	-0.13931
401.48200	0.12315	97.23294	-0.18896
451.48200	-1.8503e-002	95.56558	-0.57730
501.48200	-0.16519	90.75969	-1.08271
551.48200	-2.7215e-002	87.06635	-0.48505
601.48200	-1.2268e-002	85.33609	-0.22130
651.48200	-1.0591e-002	84.43359	-0.14990
751.48200	7.6733e-002	83.83333	-4.2020e-019
793.98200	0.11288	83.83333	-2.8363e-014

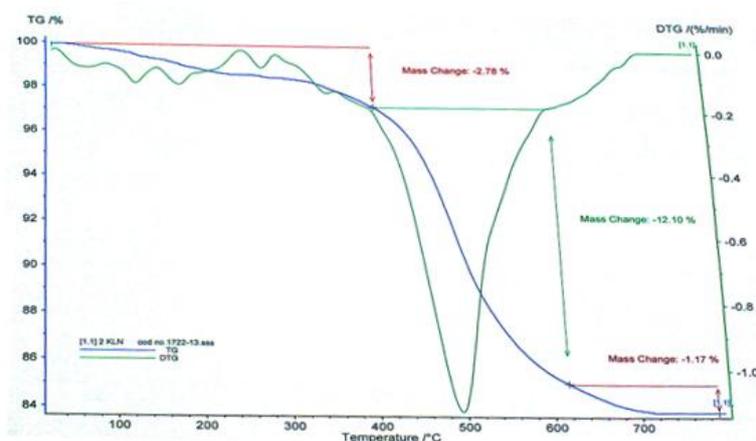


Figure 1: TG and DTG curves of kaolin

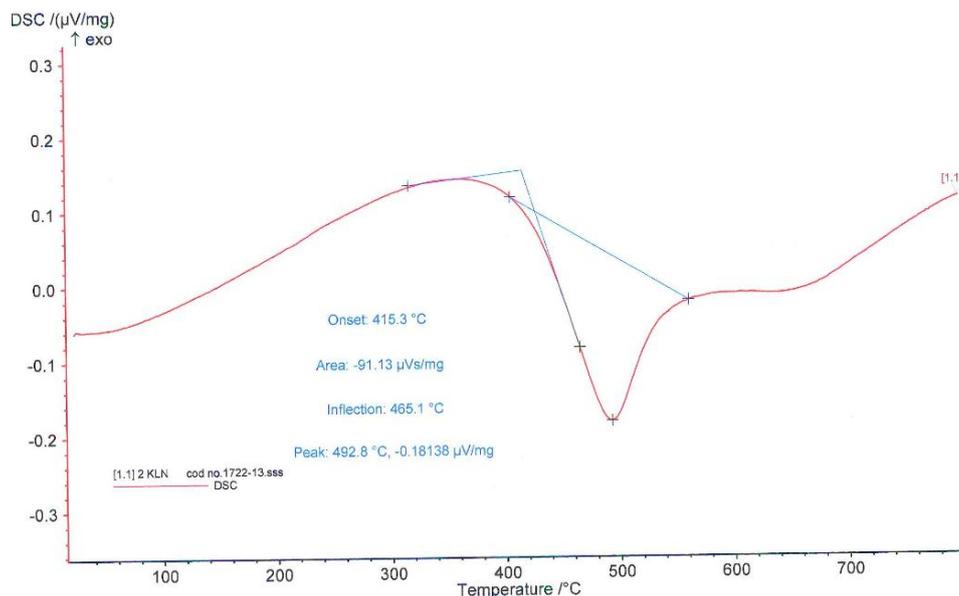


Figure 2: DSC curve of kaolin

3.5 Determination the degree of dehydroxylation (D_{tg}) of MK

In order to obtain optimal calcination parameters, the clay was subjected to thermal treatment at different heating temperatures for 2 hours. The mass loss of starting clay for given calcinations parameters and the degree of dehydroxylations is given in Table 7.

Table 7: Mass loss % and D_{tg} of MK for different calcining temperatures

Heating time	Temperature °C			TG	Chemical analysis
	550	650	750	790	
120 min	13.87	14.15	14.93	16.17	15.3
D_{tg}	0.91	0.92	0.98	0.95	

As can be seen in the Table 7, the mass loss increases for calcination temperatures of 550, 650, and 750 °C. For applied heating time at temperature 750 °C obtained value for mass loss is 14.93%. Using mass loss values during calcination, and LOI obtained by chemical analysis (M_{max}), the degree of dehydroxylation calculated by Eq. 3 are presented in Table 7. As can be seen, nearly complete dehydroxylation was achieved for temperature of 750 °C, for which the degree of dehydroxylation, D_{tg} , is 0.98. So the optimal parameters for calcination are temperature 750 °C and heating time of 120 min. This result is complying with that obtained from the thermal analysis as shown in Table 6.

There are three regions in thermal analysis can be distinguished as: the dehydroxylation region ($D_{tg} < 0.9$); metakaolinite region ($0.9 < D_{tg} < 1$); and the spinel region ($D_{tg} = 1$) [15]. In order to confirm disappearance of kaolinite peaks, after thermal treatment, the XRD patterns of starting and calcined kaolin were compared. The results are presented in Figures 3 and 4. The evident from Figure 3 that the major mineral constituents of the starting material are kaolinite and quartz. The results of XRD measurements of the calcined kaolin, selected on the base on their degree of dehydraxylation, are given in Figure 4. After thermal treatment of kaolin at temperature 750°C and heating time 120 min, characteristic peaks for kaolinite (2θ 12.41, 20.21 and 25.49°) disappear, while peaks assigned to quartz (2θ 21.22 and 27.45°) remains unchanged. This result correlates well with results of DSC/TG analysis D_{tg} as shown in Figure 4.

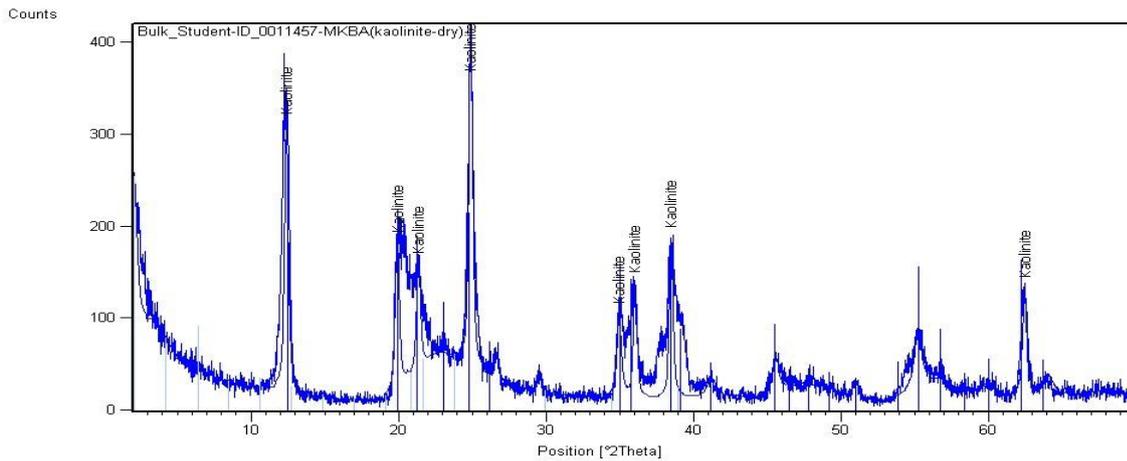


Figure 3.: XRD Pattern of Raw Kaolin

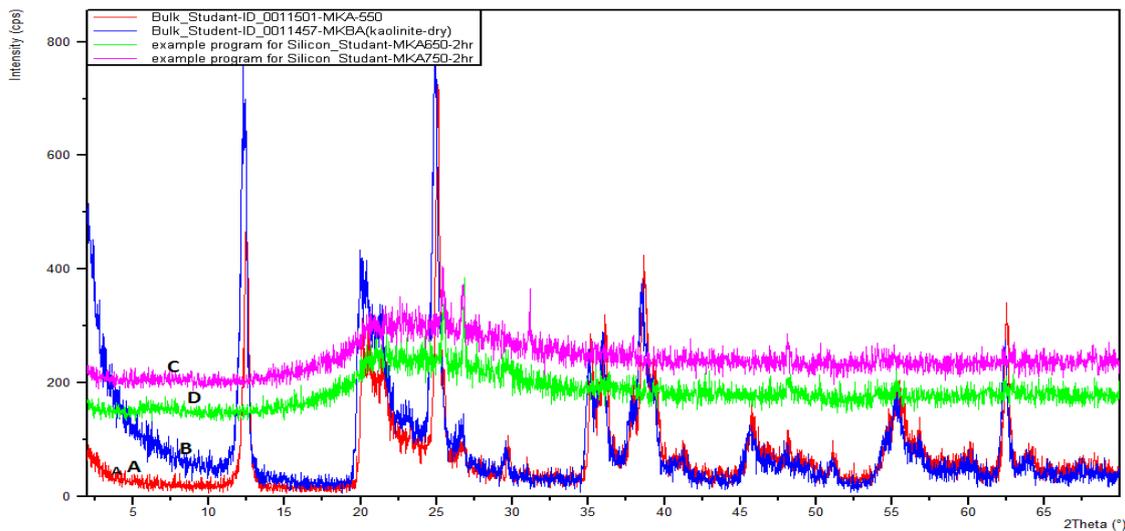


Figure 4: Combined XRD pattern of kaolin at a) raw kaolin, b) 550 °C, C) 650 °C, and d) 750 °C

3.6 Physical properties of blended mortars

3.6.1 Water consistency and setting time limits

The results presented in Table 8, indicated that addition of MK retarded to the setting time, however this retardation was negligible and was within limits as specified in [21]. It could be caused due to the adsorption of water at the surface of MK with higher surface area. The higher the proportion of MK, the higher was the adsorption of water and hence higher amount of water retarded the setting time. Most natural pozzolanas tend to increase the water requirement in the normal consistency test as a result of their microporous character and high surface area [22].

Table 8. Water consistencies and setting times for control and blended mortar

Mix	Water consistency (%)	Initial Setting time (min)	Final setting time (min)
CTR	0.320	75	150
Mmk10	33	95	180
Mmk20	34	105	200
Mmk 30	34	110	210
Mmk 40	35	120	210
IS:[21]	-	60	600

3.6.2 Compressive Strength Results of MK /OPC Blend

Table 9 and Figure 5 present the results of compressive strength tests. The results indicated that 10 and 20% addition of the MK provided 42, and 42.67 MPa, respectively, compared with 41.33 MPa of the control cubes compressive strengths tested at 28 days curing. However, at 90day curing, 10 %, 20%. and 30% addition of the MK provided compressive strength higher than reference control cubes compressive strengths. These percentages additions met the IS [19] specifications. From the results of compressive strength, the use of MK at 10%, and 20% substitutions showed minimal increase of compressive strength when compared with the compressive strength of reference mortar at 28 days age. While at 90 days age 10, 20, and 30% MK showed an increase of compressive strength over the reference. Lower strengths were obtained for those blends with higher substitution levels at 7, and 28 day. A similar growth rates to the reference mortar were observed for all substitution levels for all ages.

Table 9. Compressive strength of MMK blended mortar at 7, 28, and 90 days

Mortar Code	Age of specimen		
	days 7 (MPa)	28 days (MPa)	91 days (MPa)
MCTR	36.7	41.3	51
MMK 10	31	42	58
MMK 20	40	42	57
MMK30	34	37	55
MMK 40	32	36	50
IS: [23]	22	33	-

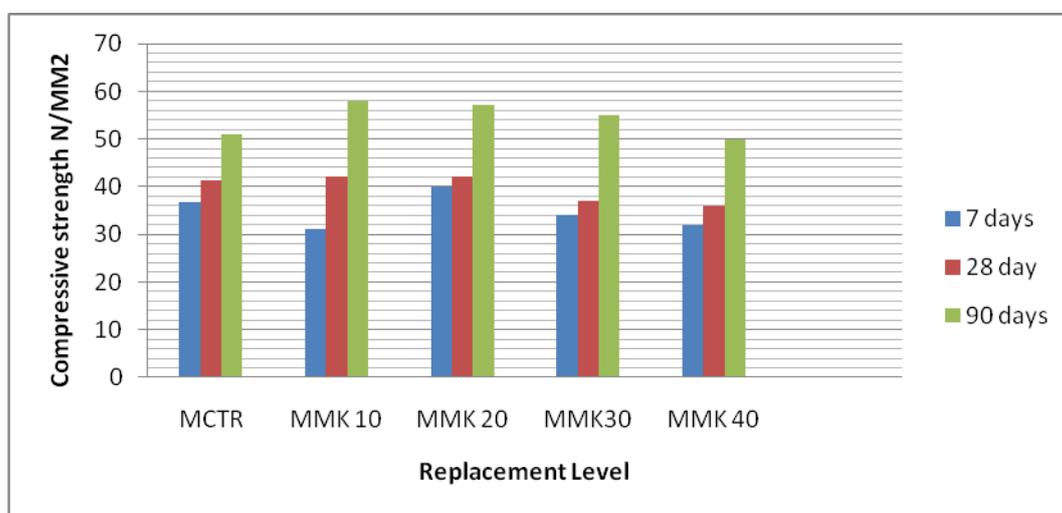


Figure 5. Compressive Strength of MMK Blended mortar

IV. Conclusions

1. The results of chemical analysis of sample showed that, the kaolin is of high purity with (SiO₂+SIO₂+Al₂O₃) content in the sum oxides of 78.95%, which are within the limitations of ASTM C-618, and IS:1344. The mineralogical composition and thermal behavior is similar to the reported compositions of other kaolinite clays.
2. The optimum calcining temperature and the degree of dehydroxilation were identified using XRD, and DSC/ DTG techniques, the calcining temperature is found to be relatively low around 750 °C, with degree of dehydroxilation Dtg equal to 0.98, this is may be due to the low content of SO₃.
3. The strength reactivity of MK with OPC at 28 days was 42 MPa, against 41 MPa for control mix, with a ratio of 102%. IS: [19] specifies a minimum of 80% of the reference for pozzolana to be used for manufacture of Portland pozzolana cement
4. The physical analysis results including Standard consistencies, and setting times for all blends showed an increase in water demand, and it increases with increasing substitution level. The results also indicated that addition of pozzolanic materials retarded the setting as shown in Table 7, however this retardation was negligible and was within limits as specified in IS: [21]. The cause may be due to the adsorption of water at the

surface of pozzolanic materials with higher surface area [22]. The higher the proportion of SCMs, the higher was the adsorption of water and hence higher amount of water which retarded the setting time. Most natural pozzolanas tend to increase the water requirement in the normal consistency test as a result of their microporous character and high surface area [22].

5. Results of compressive strength of blended cements showed that, in general, increasing the level of substitution contributed to a reduction in compressive strengths. This is especially noticeable at early ages and higher (greater than 20%) substitution levels. All blended cements showed a trend for increasing strengths with time, with the increase from 7 to 28 days smaller than the increase from 28 to 90 days, up to 40% substitution complied with the standard requirements. This allows some guide to the commercial opportunity to utilize these blends for mortars and concrete manufacture according to the end use.

References

- [1]. Muller C.J. (2005), Pozzolanic activity of natural clay minerals with respect to environmental geotechnics doctoral diss., Swiss Federal Institute of Technology, Zurich, Switzerland
- [2]. ASTM C618-(2000), "Standard Specification for Fly Ash or Raw or Natural Pozzolan for Use as a Mineral Admixture in Portland cement Concrete", American Society for Testing and Materials.
- [3]. Lea, F.M. (2004), "Chemistry of Cement and Concrete". 4 th, Ed, London, Arnold, pp. 471-632.
- [4]. Rafat, S. Khan, M.I. (2011). "Supplementary Cementing Materials ". Springer-Verlag Berlin Heidelberg
- [5]. Ridho, B. M. Darmawan, S. (2011), "Characterization of Pozzolanicity Bromo's Volcanic Ash", Proc. of International Seminar on Applied Technology, Surabaya, 218-223
- [6]. Ilic, B. R. , Mitrovic, A., Milicic, L. R. (2010), "Thermal treatment of kaolin clay to obtain metakaolin", Institute for Testing of Materials, Belgrade, Serbia , Hem. ind. 64 (4), pp. 351-356
- [7]. Aleksandra, M. , Miodrag, A., (2012), "Mechanochemical treatment of Serbian kaolin clay to obtain high reactive pozzolana", J. Serb. Chem. Soc. 77 (0), pp.1-17
- [8]. Ali, K. I., (2011), "Activation of red kaolin clay as pozzolanic material", Al-Qadisiya Journal For Engineering Sciences Vol. 4 No. 3, pp. 247-257.
- [9]. Mostafaa, N. Y. et al (2001) , "Characterization and evaluation of the pozzolanic activity of Egyptian industrial by-products , Silica fume and dealuminated kaolin", Cement and Concrete Research, 31 pp. 467 -474.
- [10]. Justic, J. M. (2005), "Evaluation of metakaolins for use as supplementary cementitious materials", MSc thesis, Georgia Institute of Technology .
- [11]. Mohamed , A.A. , Ganjian, E. (2013), "A Study on the Effect of addition of thermally treated Libyan Natural Pozzolan on the Mechanical Properties of Ordinary Portland Cement Mortar" · International Journal of Science and Technology, Volume 3 No.1, pp. 79-84.
- [12]. Ray, L. F., Erzsebet, H. , Éva, M., (2003), "Slow transformation of mechanically dehydroxylated kaolinite to kaolinite - an aged mechanochemically activated formamide-intercalated kaolinite study", Thermochimica Acta, 408(1-2), pp. 103-113
- [13]. Badogiannis, E. Kakali, G. , Tsivilis, S., (2005), "Metakaolin as supplementary cementitious materials", Optimization of kaolin to metakaolin conversion. Journal of Thermal Analysis and Calorimetry, Vol. 81 pp. 457-462.
- [14]. Kovler, K., Shvarzman, A. , Grader, G., Shter, G., (2001), "Influence of chemical and phase composition of mineral admixture on their pozzolanic activity", Advances in concrete research, V. 1, pp. 1-7.
- [15]. Rahier, H. ,Van Mele, B.,(2000), "Influence of the degree of -dehydroxylation of kaolinite on the properties of aluminosilicates glasses", journal of thermal analysis and calorimetry vol., 62 ,pp417-427.
- [16]. Indian standard (IS 650: 1991)"Specification of standard sand for testing cement"
- [17]. Indian standard (IS :1727-1967)" Methods of test for pozzolanic materials"
- [18]. Indian standard (IS:4031-1996) part 6- "Methods of physical tests for hydraulic cement, determination of compressive strength of hydraulic cement (other than masonry cement)".
- [19]. Indian standard, (IS: 1344-1981), "Specification of calcined clay, pozzolana."
- [20]. Indian standard (IS 8112-1989)" 43 Grade ordinary Portland cement specification"
- [21]. IS 4031 : Part 4 : 1988 Methods of physical tests for hydraulic cement: Part 4 Determination of consistency of standard cement paste
- [22]. ACI 232.(2000), "Use of raw or processed natural pozzolans in concret.", ACI Committee 232 Report, American Concrete Institute, Farmington Hills, MI.p.4.
- [23]. Indian standard (IS 1489-1967),"Specification for Portland- Pozzolana Cement"

El-Sharif M. Ibrahiem . et. al. "Pozzolanic Characteristics of Local Kaolin for Use in Blended Cements." *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, 18(4), 2021, pp. 39-46.