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Lime –Metakaolin Interaction

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ABSTRACT The standard mix ratio of lime: pozzolana specified by all standards is 1:2 by weight to produce lime pozzolan cement (LPC) with the minimum required strength of 4 MPa. This ratio may be affected by many factors such as the quality of lime and pozzolana, in adition to the quantity of amorphous silica in pozzolana. In this paper a local kaolin and lime were investigated for their chemical, physical, mineralogical, and thermal properties, using various techniques such as XRF, DTG/DSC, and XRD. The produced metakaolin (MK) and hydrated lime (CH) were first tested for their reactivity, then different ratios of 1:2, 1:3, and 1:4 (lime: metakaolin) were tested to determine the optimum mix ratio of (LPC). The chemical, physical, and mineralogical analysis of samples showed their congruent with standard specifications adopted. The chemical analysis results showed that the local kaolin has composition with a SiO2+Al2O3+Fe2O3 content of 79.96%. The reactivity of MK toward CH is found to be within the limitation of standards. The mortar samples, made with a binder of ground MK and CH, developed a 28 days compressive strengths of 4.9, 14, and 16 MPa, for 1:2, 1:3, and 1:4 (CH: MK) respectively. These findings suggest that LPC can be produced with high compressive strength if an optimum lime to pozzolana ratio is achieved.

Keywords: compressive strength, lime pozzolana cement, metakaolin, pozzolanic reactivity.

1. INTRODUCTION

The purpose of studying pozzolan / lime blends (lime- pozzolan cement) is to better understand the reaction between one of the hydration products of Portland cement, calcium hydroxide, without the interference of the other compounds. Such reaction is characterized by the decrease of the quantity of calcium hydroxide and the formation of a hydration product. Pozzolanas are long known to be able to harden by reaction with aqueous calcium hydroxide solutions. In most applications, calcium hydroxide is supplied by Portland cement clinker, i.e. the pozzolanas are used as additions to produce blended cements. However, under favourable conditions it is sufficient to activate ground pozzolanic powder by addition of only lime to initiate pozzolanic reaction [1]. This means that lime instead of Portland cement can be used to produce binders from natural pozzolans.

2. BACKGROUND

Metakaolin (MK) is a supplementary cementing material (SCM) that conforms to ASTM [2] Class N pozzolan specifications. MK is unique in that it is not the by-product of an industrial process nor is it entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications. Unlike by-product pozzolans, which can have variable composition, MK is produced under carefully controlled conditions to refine its color, remove inert impurities, and tailor particle size [3]. As such, a much higher degree of purity and pozzolanic reactivity can be obtained. MK has great promise as an SCM, as it can improve many properties of concrete while also reducing cement consumption.

Metakaolin is produced by heat-treating kaolin. The main process important for production high reactivity pozzolana from kaolin clay is calcination. The heating process drives off water from the mineral kaolinite

($Al_2O_3.2SiO_2.2H_2O$), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate ($Al_2O_3.2SiO_2$), metakaolinite. The process is known as dehydroxylation, [3], and may be presented by simple equation:

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{\Delta} Al_2O_3.2SiO_2 + 2H2O\uparrow \quad ....(1)$$

The thermal transformation of kaolinite, which has been the subject of a large number of investigations [4] - [10], has shown that the heating parameters such as temperature, heating rate, and time, as well as cooling parameters (cooling rate and ambient conditions), significantly influence the dehydroxylation process. The major quantitative criterion for evaluating the performance of kaolinite by thermal treatment is a degree of the dehydroxylation, Dtg:

$$Dtg=(M/M_{max}) \quad ... \quad ....(2)$$

where M and M_{max} are residual and maximum sample mass loss, respectively. The dehydroxylation of pure kaolinite (39.5% Al_2O_3, 46.5% SiO_2 and 14% H_2O) in ambient atmosphere results in mass loss of about 14% and Dtg = 1, which corresponds to mass in bound hydroxyl ions in kaolinite [11], [12] .

In this study the optimum calcining temperature to covert kaolin into metakaoline was obtained using (DSC/DTG) techniques, and XRD .There are three regions in thermal analysis can be distinguished : the dehydroxylation region (Dtg <0.9), the metakaolinite region(0.9<Dtg<1),and the spinel region (Dtg=1) [13].

In Sudan Kaolinite clay deposits are known to occur in several locations. Deposits which were geologically described include those Kaolinite deposits located in the basement complex in Derudeb area in the red sea hills, in J. Hazim in Northern Kordofan, J.Nakashush NW Sudan, J. Um Ali North of Shendi, J. Tawiga in NW Sudan. Merkhiyat Hills NW of Omdurman, kaolinite paleosols at El Atrun area, and the kaolin deposits of Gedarif – Showak district in Eastern Sudan [14]. Kaolin from Dikera area in Eastern Sudan has also studied and characterized [15]

3. MATERIALS

A. Materials

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

B. Sand

River sand procured from Wadi Nyala, was used in present study. The sand was washed, dried, and sieved into different fractions, it was standarized according to IS [16] to three grades - fine (90 µm to 500 µm), medium (500 µm- 1mm) and coarse (smaller than 2mm-and greater than 1mm) fractions.

C. Metakaolin (MK)

The Kaolin sample used in this investigation was collected from Rahad Abiad area 40 km to the south of Nyala tawn (latitude 12°31'28.65"N, longitude 24°17'7.39"E). The sample was first studied for chemical composition.. Then, the obtained MK was pulverized and sieved to grain size of less than 63 µm, and then characterized using chemical, physical, and x-ray diffraction analysis.

D. Lime

Lime used in this study is Hydrated lime (CH), the source of raw material for the production of lime (CH) is the Marble procured from Juruf area 60 km North to Nyala city latitude (12°32'1.12"N) longitude (25° 1'30.82"E). The raw material was calcined at 975 c for 3 hours, the produced quick lime (CaO) was slacked and ground to pass 90 micron sieve.

E. Water

Water from the public main supply was used for the production and the curing of the mortar cubes.

4. METHODS

A. Testing of pozzolanic reactivity

As a primary step in this investigation, the pozzolanic reactivity of MK with lime was examined in the term of compressive strength following the procedures described in [17]. For determining the reactivity of the pozzolanic material with hydrated lime, the standard mortar cubes of 50 mm were casted, cured, and tested accordingly. The mix of CH: MK: standard sand in proportion (1: 2M: 9) by weight was used, where M :is the ratio of Specific gravity of pozzolana to Specific gravity of lime. The details of mix proportions are shown in Table I.

TABLE I: MIX PROPORTIONS FOR POZZOLANIC REACTIVITY WITH CH FOLLOWING [17]

Lime – pozzolana mix	
Component	Amount (g)
Lime – Ca(OH)2	150
MK	138
Standard sand	1350
flow	70 ± 5

B. Preparation of blended mortar

Lime was blended with, metakaolin in (1:2, 1:3, and 1:4) (lime: metakaolin) proportions. The details of mix proportions are shown in Table II

TABLE II: MIX PROPORTION FOR BLENDED MORTAR

Mortar code	Blending Ratio (By Weight %)		B:AG By weight	No of Specimens	Test age
	MK	CH			Day
L-MK 12	67	33	1:3	9	7,28
L-MK 13	75	25	1:3	6	7,28
L-MK 14	80	20	1:3	6	7,28

5. RESULTS AND DISCUSSIONS

A. Chemical Properties

The chemical analysis results of metakaolin presented in Table III , indicated that the principal oxides of Silica (SiO2), Alumina (AI2O3) and Iron (Fe2O3) were substantially present in the sample investigated with the sum oxides of 79.92,. The analyses also showed the presence of minor element, while the LOI of the sample evaluated was 15.3%. These results are within the limitations of [18] and [2]

B. Physical properties of materials

The physical properties such as specific gravity and fineness (by sieving and specific surface area) of the, MK, and lime used in this study were determined in accordance with IS [19], (Table IV)

C. Results of TG/DSC and XRD Analysis OF MK

Thermal behaviors of the raw Kaolin are presented in the Figures 1 and Table V. The main changes revealed by TG and DTG analysis are as follows:

At temperatures below about 200 °C release of water absorbed in pores and on the surfaces occurs. Between 200 and 450 °C, 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 - in our case 751 °C ,Table V. - 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 To = (dm/dTmax) and the weight loss onset temperature (Tonset). The former refers to the temperature of the maximum rate of oxidation, while the latter refers to the temperature when oxidation just begins.

D. Determination of the degree of dehydroxylation Dtg 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 VI.

TABLE VI: MASS LOSS % AND DTG OF MK FOR DIFFERENT CALCINING TEMPERATURES

Heating time	Temperature ^{0} C			TG	Chemical analysis
	550	650	750	751	
120 min	13.87	14.15	14.93	16.17	15.3
D_{tg}	0.91	0.92	0.98	0.95	

TABLE III: CHEMICAL COMPOSITION OF KAOLIN

Material	Chemical Composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na2O	K_2O	LOI
MK	43.66	35.29	0.97	1.79	0.255	0.063	0.29	0.04	15.3

TABLE IV: PHYSICAL PROPERTIES OF MK AND CH

Material	Specific Gravity	Fineness measured			Fineness Requirements
		Passing sieve No %		Blaine Surface area	[18]
		90 micron	45 micron	cm^2/g	cm^2/g
MK	2.6	100	87	7688	3250
CH	2.4	98	-	2028	

TABLE V: 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

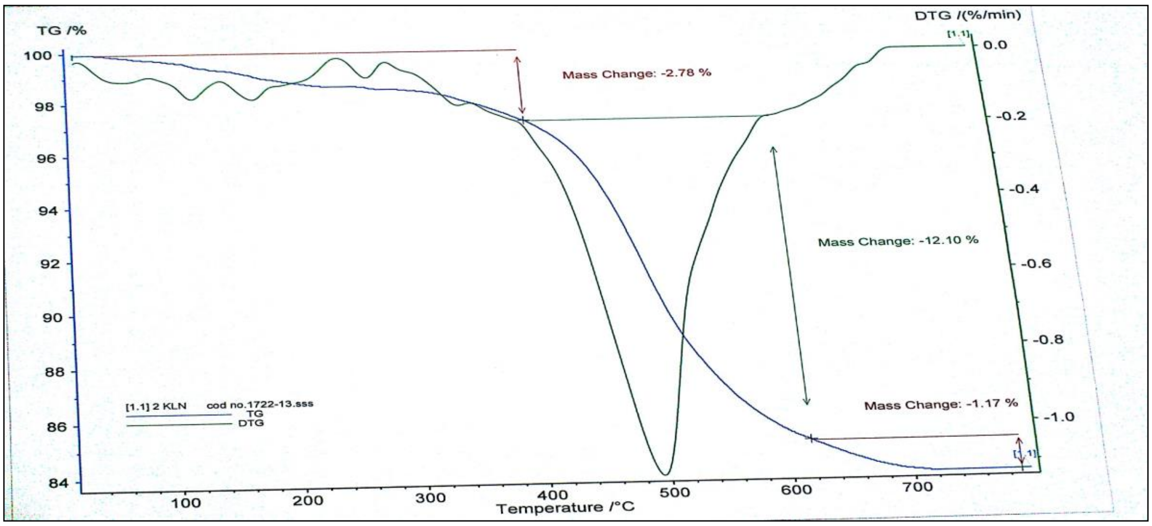

Fig. 1.TG and DTG curves of Kaolin

As can be seen, for calcination temperatures of 550, 650, and 750 °C, mass loss increases. 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 (Mmax), the degree of dehydrohylation calculated by Eq. 2 are presented in Table VI. As can be seen, nearly complete dehydroxylation was achieved for temperature of 750 °C, for which the degree of dehydroxylation, Dtg, 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 (Table V)

There are three regions in thermal analysis can be distinguished: the dehydroxylation region (Dtg <0.9), the metakaolinite region (0.9<Dtg<1),and the spinel region (Dtg=1) [13].

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 2 and Figures 3. It is evident from Figure 2 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 3. 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 Dtg (Figure 1).

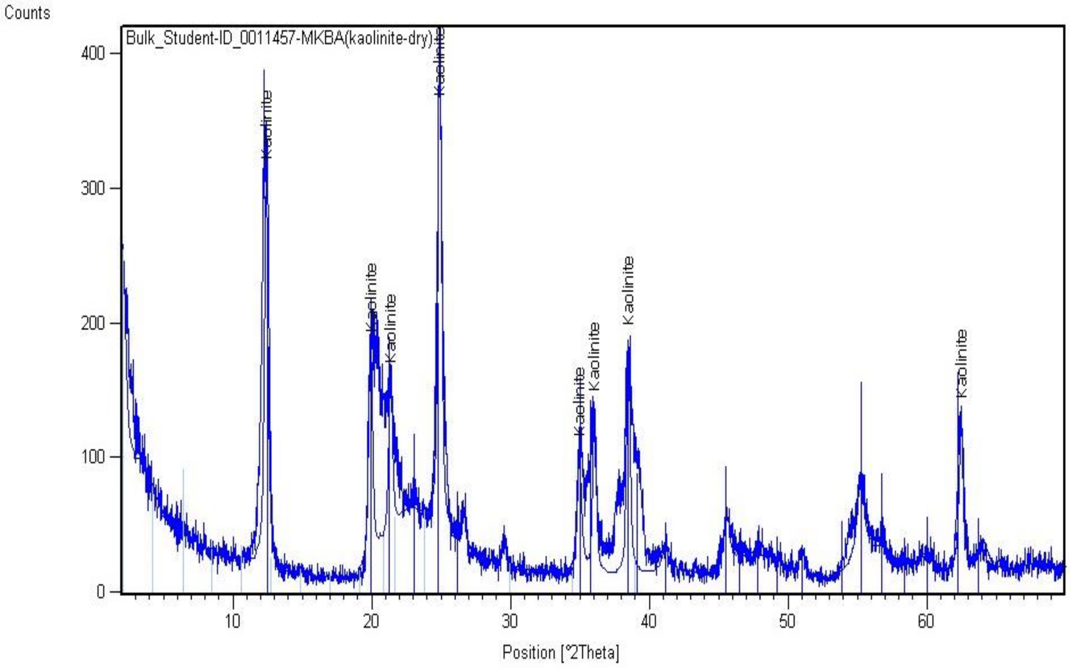

Fig. 2. XRD Pattern of Raw Kaolin

E. *Reactivity test results*

The reactivity of MK toward lime is measured through the compressive strength of standard mortar tests according to [17]. The result of the MK reactivity with lime was 4.9 Mpa. at age of 8 days, IS-[18] required a minimum of 4.0 MPa.

F. *Results of Lime / MK Blends*

Results presented in Table VII, showed that, the compressive strength of lime- pozzolana blends is greatly affected by the quality of pozzolana, and the magnitude of the strength development increase with increase of pozzolana: lime ratio. At 28 days curing . The compressive strength of CH/ MK blends were 4.9, 14, and 16 MPa. for the ratios 1:2, 1:3, and 1:4 respectively. It's clear that, the magnitude of the strength development of MK blends increased dramatically from 1:2 to 1:3 ratio, from 4.9 to 14 MPa, and to 16 MPa for 1:4 ratio.

TABLE VII: COMPRESSIVE STRENGTH OF LIME/METAKAOLIN BLENDED MORTARS

Mortar code	Compressive strength MPa		
	7 days	28 day	91 days
L-MK 12	4	4.9	6.7
L-MK 13	9	14	-
L-MK 14	11	16	-
[20]	2	4	8

Therefore, MK is more reactive with lime. It's generally agreed that, the production of C-S-H, depends on the CH consumption by the amorphous silica presented in pozzolana, and the degree of consumption also depends on type of pozzolana

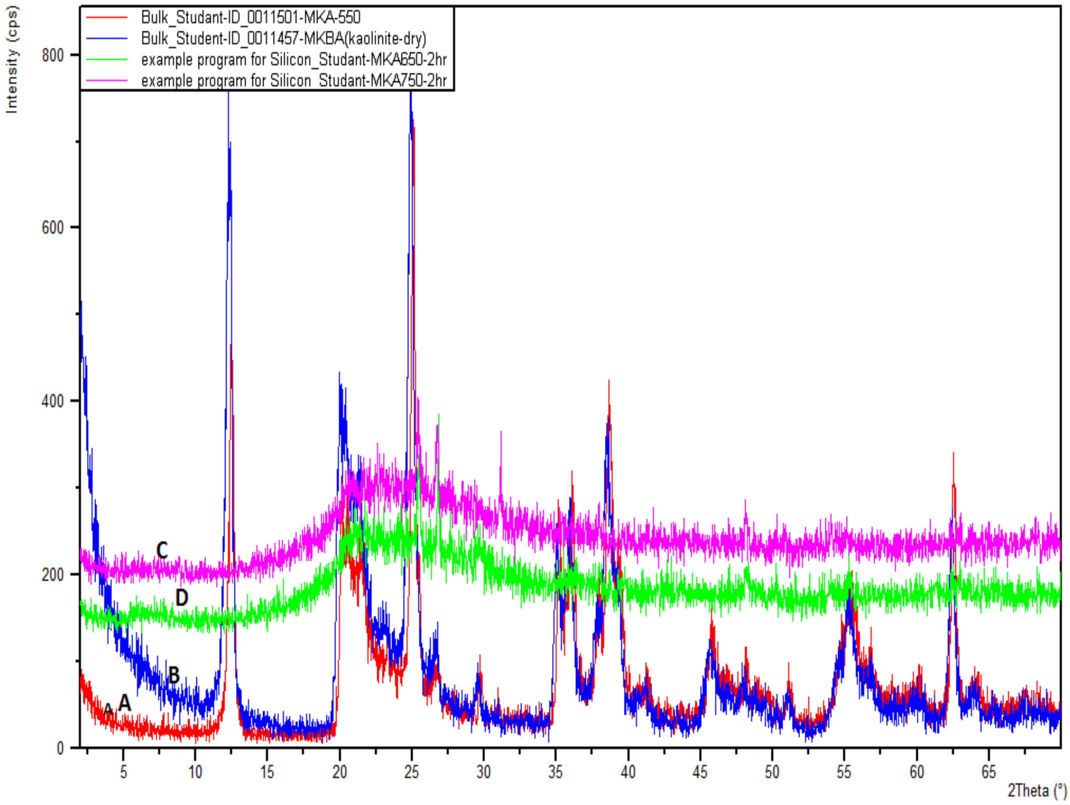

Fig. 3. Combined XRD pattern of kaolin at a) raw kaolin, b) 550 ^{0}C, C) 650 ^{0}C, and d) 750 ^{o}C

6. CONCLUSIONS

1. The results of chemical analysis of sample showed that, Rahad Abiad kaolin is of high purity with (SiO_2+ Al_2O_3) content in the sum oxides of 78.95%,which are within the limitations [2], [18].
2. The mineralogical composition and thermal behavior is similar to the reported compositions of other kaolinite clays.
3. The calcining temperature is found to be relatively low around 750 ^{0}C,with degree of dehydroxilation Dtg 0.98, this is may be due to the low content of SO_3.
4. The strength reactivity of MK with lime was 4.9 MPa, [18] specifies a minimum of 4.0 MPa.
5. The compressive strength results of lime-pozzolana blends is greatly affected by the quality of pozzolana ,and the magnitude of the strength development increase with increase of pozzolana: lime ratio,
6. This high strength give a new recomendation to the applications of lime – metakaolin mixure in mortars, plasters, and even the manufacturing of bricks.

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