

# A Study on Portland Limestone Cement Blended with Animal Bone Ash and Metakaolin

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## To cite this article:

Jarumi Luka, Tijani Mohammed Isah, Olubajo Olumide Olu. A Study on Portland Limestone Cement Blended with Animal Bone Ash and Metakaolin. *American Journal of Chemical Engineering*. Vol. 10, No. 5, 2022, pp. 103-115. doi: 10.11648/j.ajche.20221005.12

**Received:** October 13, 2022; **Accepted:** November 7, 2022; **Published:** November 22, 2022

**Abstract:** The increased discriminate disposal of agricultural wastes from slaughter houses has become a serious concern resulting in contamination of human environment, thus there is a need to consider utilizing such waste to solve the challenges faced in the production of cement. This study examines the impact of cement replacement with Animal Bone Ash (ABA) and Metakaolin (MK) up to 12.5 wt.% on the physical and mechanical properties of blended cement. The consistence, setting times and soundness test were conducted on thirty-six ABA- MK-cement pastes via Vicat and Le Chatelier apparatus respectively while the mortar strength tests were conducted using a compression testing machine at 3, 7, 28, 60 and 90 days. The chemical analysis for MK revealed that the sum of oxides of silicon, aluminum and iron content was greater than 70% (97.06 wt.%) and thus, a good pozzolan according to ASTM C 618 whereas ABA was less than 70%, but could be regarded as a cementitious filler/additive. Results revealed ABA comprising mainly lime (53.86 wt.%) and Phosphate (40.96 wt.%) from X-ray analyses which agreed with X-ray diffractogram and scanning electron microscopy analyses. Results indicated a slightly higher water consistency between 32 to 36%; a higher volume expansion (unsoundness) between 0.5 – 5 mm whereas the accelerated initial setting time (260 to 126 mins) and retarded final setting time (183 to 315 mins) as the cement replacement was gradually increased. An increase in the blending ratio led to a slightly higher water consistency between 32 – 36%; increment in the volume expansion from 0.5 – 5 mm and lower setting times. Most of the cement blends exhibited enhanced 28 days mortar strengths in comparison with control despite diminution of clinker content due to pozzolanic activity. An increase in strength gain for all cement blends and control were experienced as the curing days were extended despite clinker diminution. The highest strength gain for various testing days and comparison with control: 28.33 N/mm<sup>2</sup> (106.5%), 32.42 N/mm<sup>2</sup> (109.9), 36.88 N/mm<sup>2</sup> (122.61), 41.31 N/mm<sup>2</sup> (120.37) and 50.91 N/mm<sup>2</sup> (122.35%) respectively.

**Keywords:** Metakaolin, Animal Bone Ash, Consistence, Setting Time, Soundness and Compressive Strength

## 1. Introduction

The management of agricultural wastes from slaughter houses is of great concern as its effluent can pollute water and land bodies [1]. Improper waste management which includes municipal solid waste, burning as well as incineration, clogging of drains indiscriminate dumping [2, 3] which could be detrimental resulting in severe ecological problems to the health of living beings and cause pollution of water and air as well as ozone layer depletion [4]. This demands the emerging need for an effective and safe disposal

method to reduce the spread of diseases following animal slaughtering. In light of the state of the production of slaughterhouse and the impact of solid waste exposure in terms of air, water, and soil pollution and the associated health challenges due to improper solid waste management practices. The potency of these solid wastes and the various waste-to-energy technologies that have been employed for effective management and resource utilization of wastes generated from slaughter houses.

The use of these industrial waste materials provides the potential to solve disposal issues and significantly reduce in demand on the natural resources. The industrial waste

generated could either be employed either partial or full cement replacement. Similarly, the replacement of cement will reduce pressure on the amount of limestone as raw materials obtained from the land excavation [5, 6]. In addition, construction industry in Nigeria is growing fast and attempts are being made to utilize the waste materials as alternative materials in the construction field due to the demand for homes and commercial spaces [7]. The high demand for waste products seems to provide a solution to ecological problems which are recyclable and cheaper [6, 8]. Furthermore, an equivalent quantity of carbon dioxide released and ordinary Portland cement manufactured. The carbon dioxide emission act is a pollutant in the environment [9] and it is on this note that the search for cheaper substitute to OPC becomes necessary.

Cement is considered a binder employed in construction which sets, hardens and adheres materials or surfaces together and is of great importance to mankind. Its importance can be seen in the area of shelter provision, construction of roads and bridges for transportation, construction of dams for irrigation and hydro-electric power station, etc. [10]. The sustainability issue in the construction sector has been a major problem for several decades arising from concerns in employing virgin materials and release of green-house gases during manufacturing [11]. The huge quantity of concrete required in the construction sector in which cement is a major constituent has steered the growing interest to employ the use of blended cements due to its benefits ranging from reduction in release of CO<sub>2</sub>, reduced energy requirement and increased productivity [11-13]. The effective utilization of materials and reduction of cost in construction industry, require the use of ternary cements that are made with Portland clinkers and two cementitious materials (ABA & MK) as a better option in the production of an economically good cement blend. The use of various cementitious materials in recent decades to improve the concrete quality in terms of enhanced strength, durability and workability [14]. The combination of metakaolin (MK) and animal bone ash (ABA) with Portland cement could help to produce a cement-based material which could be advantageous in the cement industry. According to Bih *et al.* [15], ABA incorporation could compensate for microcracks as well as increase in the compressive strength with one of the obvious advantages is its contribution to early strength since ABA composition is similar to limestone. According to Olubajo *et al.* [16] and Georgescu and Saca [12], limestone inclusion was obvious by improved early strength, while silicon oxide presence in MK led to an enhanced latter strength, resulting in adequate strength development, soundness and setting time of the new improved cement blend stemming from technical benefit of cement blends [17, 18].

Clay as an alternative inorganic binder is growing and its abundance having promising properties as a cost effective and ecofriendly material [19-21]. They are rich in alumina and clay resulting in pozzolanic reactions under appropriate conditions [22]. It has studied that it could exhibit excellent pozzolanic activity by calcination or surface modification [19, 23]. Metakaolin comprises of alumina and silica which are

pozzolanic precursor materials with silica offering improved durability while alumina contributes to the enhanced strength [24]. Metakaolin amongst the commonly employed calcined products of kaolinite which is an aluminosilicate anhydrate (Al<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) obtained by calcination. Metakaolin is dehydroxylated clay mineral (kaolinite) obtained by calcining at temperature between 500 – 800°C which has been employed as an effective pozzolans in binary and ternary composition with varying successes of enhanced strengths, diminished permeability and efflorescence potency, enhanced durability and higher chemical resistance, etc. [17, 22, 25]. Bone ash is a white material with chemical formula Ca<sub>5</sub>(OH)(PO<sub>4</sub>)<sub>3</sub> bones which comprises of 55.82% of CaO and 42.39% of P<sub>2</sub>O<sub>5</sub> and variation in composition is dependent on the bone type. Its density around 3.10 g/ml and melting point of 1670°C. Animal bone ash finds application for agricultural purposes as fertilizer; metallurgy as a cupellation (process of removal of precious metals from base metals) owing to bone ash extremely high porosity, calcareous structure as well as its high melting point. The content of CaO makes it useful as an ingredient in the production of cement [26].

Tsivilis *et al.* [27] and Georgescu & Saca [12] indicated that incorporation of calcite into cement matrix resulted in increment in the early strength properties of the blend due to nucleation effect from high surface area of limestone-cement blend coupled with the filler effect of fine calcite grains. Whereas, the later strength of cement blended with limestone experienced a decline in its strength compared with control, cement incorporating calcareous fine powder not only did not improve strength properties but also somewhat reduced in comparison with control Portland cement [28]. Several literatures consulted revealed that several researches have been conducted on the utilization of biomasses such as saw dust ash, coal bottom ash, rice husk ash, orange peel ash etc. to improve some of the physicomaterial properties of ternary cement [13, 16, 17, 29, 30]. However, no research work is yet to be done on the improvement of the physicomaterial properties of ternary cement using calcined animal bones which is rich in lime and phosphate obtained from agricultural waste. Therefore, the study is focused on investigating the effect of pulverized ABA and MK on the physical and mechanical properties of blended cement such as water consistency, loss of ignition, soundness, initial and final setting times, mortar strength.

## 2. Materials and Methods

Replacement of Portland limestone cement with ABA and MK were carried out to obtain ternary cement blends at cement replacement of 2.5 -12.5 wt.% at interval of 2.5 wt.%. Table 2 indicates thirty-six different ternary cement blends prepared using Portland limestone cement, ABA and MK at various proportions. A Nigerian commercial Portland limestone cement type CEM II A-L 42.5 R according to Nigeria Industrial Standard (NIS) was supplied by Dangote cement company and used as a control. Animal bones were collected from slaughter house located in Yelwa, in Bauchi

metropolis, Bauchi State. ABA was obtained from calcination in a blast furnace at a temperature of 1000°C and 1 atm for 5 hrs. The calcined bones were cooled and crushed using mortar and pestle, grinded with a grinder and sieved using a 90-micron sieve. Raw kaolin was obtained from Alkalari village which was beneficiated and calcined at a temperature of 650°C at 1 atm for 3 hrs and sieved using 90-micron sieve. The required water of standard consistency, initial and final setting time were determined according to the European standards EN 196 – 3: [31] using Vicat apparatus while the soundness was determined using Le Chatelier apparatus according to B IS 4031 [32]. The compressive strength test was carried out on mortar samples mixed using water: binder: sand at a ratio of 1:2:5. The mix was then cast in the oiled mold of 50 mm cubes after which were compacted after vibrating with a jolting machine for 2 minutes. The moulds were then surface smoothed and covered with an impervious sheet to avoid evaporation and cured at room temperature for 24 hours, followed by demolding of the cubes. The resultant demoulded cubes were then placed in a curing tank containing distilled water for strength testing at the required ages of 3, 7, 28, 60 and 90 days for mortar compressive strength using the Tonic Technic compression machine.

### 3. Results and Discussion

#### 3.1. Characterization of ABA and MK

The chemical and mineralogical analyses were determined via X-ray Fluorescence spectrometer (XRF) and X-ray Diffractometer (XRD) respectively. The physical characteristics and chemical composition of PLC, ABA, and MK were tabulated in Table 1.

##### 3.1.1. Results of Chemical Analysis for ABA and MK with XRF

The chemical analysis of ABA tabulated in Table 1, indicated 40.96 wt.% of  $P_2O_5$  and 53.86 wt.% of CaO with summation of  $Fe_2O_3$ ,  $Al_2O_3$  and  $SiO_2$  was found to be 1.26% which is less than 70% minimum requirement according to ASTM. C618 [33]. Thus, oxide composition of ABA does not meet the prerequisite to be considered as a pozzolan, but can be considered as a filler because it possesses a high lime content of 53.86 wt.%. The ABA's specific gravity and bulk density was determined to be 1.29 and 1.13 g/cm<sup>3</sup> respectively which was lower compared with ordinary Portland cement and Portland limestone cement's specific gravities of 3.05 and 3.15 respectively [34, 50], thus, ABA can be regarded as a lightweight and voluminous material.

**Table 1.** Chemical and Physical Composition of Portland limestone cement, Animal bone ash and Metakaolin

Compound	PLC wt.%	ABA wt.%	MK wt.%
SiO <sub>2</sub>	12.39	0.71	51.8
Al <sub>2</sub> O <sub>3</sub>	4.20	0.56	43.75
Fe <sub>2</sub> O <sub>3</sub>	1.95	0.025	1.51
CaO	43.14	53.86	0.54
MgO	0.74	1.61	0.11
K <sub>2</sub> O	1.03	0.05	0.20
Na <sub>2</sub> O	0.63	0.86	0.04
TiO <sub>2</sub>	0.19	1.32	2.05
CuO	-	0.029	-
P <sub>2</sub> O <sub>5</sub>	0.18	40.96	-
Mn <sub>2</sub> O <sub>3</sub>	0.10	-	-
Sum of concentration	99.32	100	100
Physical properties			
LOI%		0.95	1.29
Specific gravity	3.05	1.29	2.58
Bulk density g/cm <sup>3</sup>	-	1.13	0.52

The Loss on ignition (LOI) of ABA was determined as 0.95% which satisfies the ASTM requirement for LOI which should not exceed 12%. The main constituents of MK are silica (51.8 wt.%), alumina (43.75 wt.%) while ferric oxide (1.51 wt.%) is a minor constituent. The sum of silica, alumina and ferric oxide gave higher than 70 wt.% (97.06 wt.%). Thus, MK can be classified as a good pozzolanic material according to ASTM C618 [33]. The combined oxide of  $Fe_2O_3$ ,  $K_2O$ ,  $TiO_2$ ,  $MnO$  and  $CaO$  were less than 10% indicating that MK possesses a high refractive index [35]. It was observed that the silica alumina ratio of the metakaolin obtained was 2.0 which is in accord with Olubajo et al. [51] which is agreement with MK chemical formula. The MK specific gravity was determined at 2.58, which agreed with El-Adnamy et al. [36] and Olubajo et al. [17] values. The LOI of MK met the ASTM prerequisite of below 12 wt.%

with a LOI of 1.29%.

##### 3.1.2. Results of Mineralogical Composition for ABA and MK with XRD

Figures 1 and 2 present the X-ray diffractogram of ABA and MK respectively. It could be observed from the diffraction spectra of ABA indicated characteristic peaks of Hydroxylapatite, Quartz, Apatite, Chlorapatite, Brushite, Gamet and lime phases respectively with Hydroxylapatite comprising the major crystal phases of ABA at 2θ of 12.0, 27.0, 33.0, 35.0, 40.0, 47.0 depicting the maximum peak. This implied that the sample is basically ABA due to high content of Hydroxylapatite. This observation is similar to the finding by Oriyomi et al. [37] and Bih et al. [15], whose XRD result showed high peaks corresponding to Hydroxylapatite.

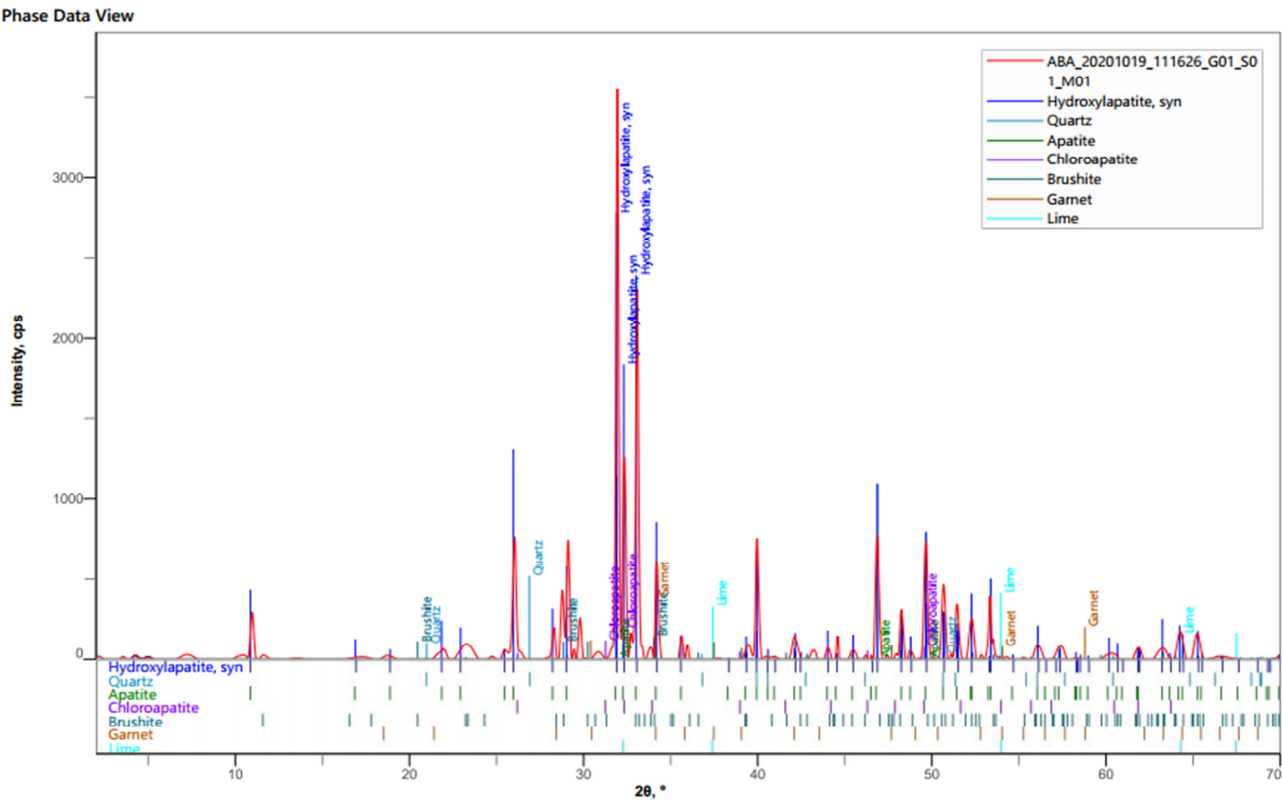


Figure 1. X-ray Diffractogram for ABA.

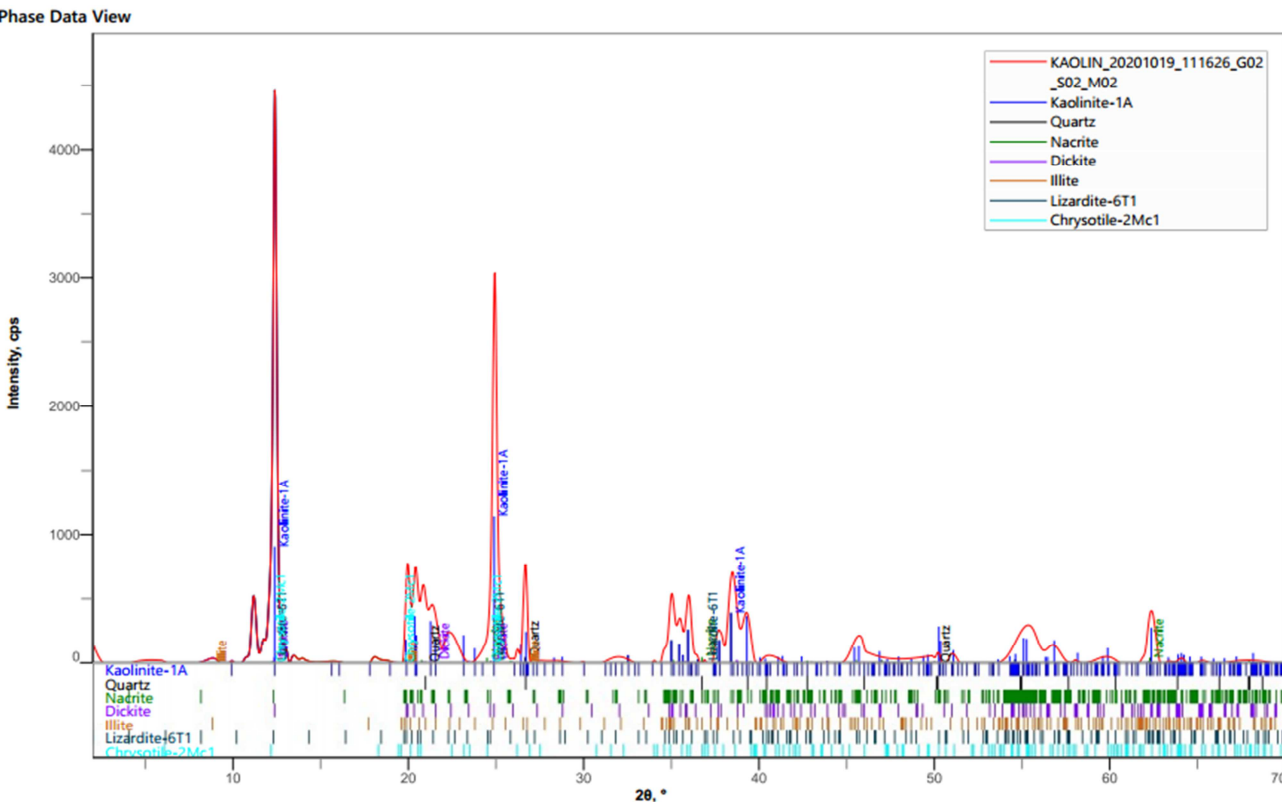


Figure 2. X-ray Diffraction Pattern for MK.

The X-ray diffractogram of MK revealed kaolinite present coupled with quartz and amorphous aluminum silicate phases, with kaolinite and quartz comprising the two main crystal phases of MK at 2θ of 12.4, 27.3, 33.6, 47.9. The X-ray

diffraction and the chemical analysis of Mk were consistent which agrees with Olubajo *et al.* [17] and Bih *et al.* [15]. The amount of penta-coordinated aluminum ions produced during the process of dehydroxylation affects MK reactivity [38].

Figures 3 (a) and (b) depict the SEM micrograph of ABA

and MK respectively. The presence of lime for the micrograph of ABA was evident by light colored patches which agrees with Younsei *et al.* [39] and Bih *et al.* [15]. The result obtained from the XRF analysis of ABA and MK were consistency with the Scanning Electron Microscopy – Electron Dispersive X-ray (SEM-EDX) analysis as shown in Figure 4.

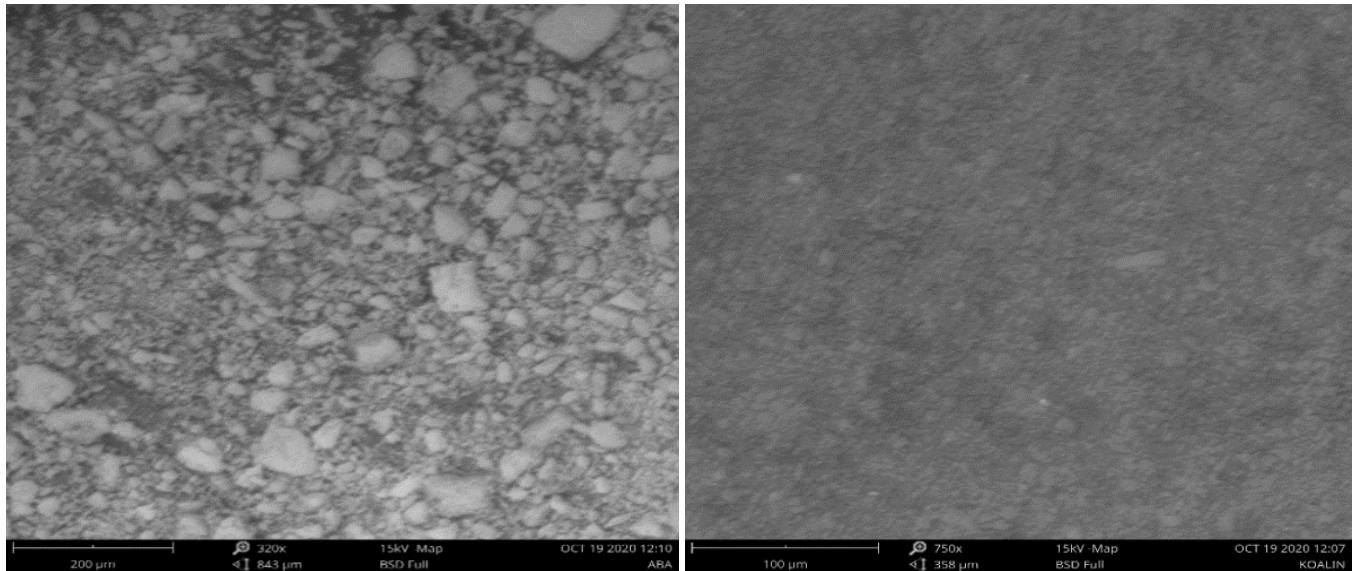


Figure 3. SEM micrograph of (a) ABA and (b) MK.

The EDX analysis indicated Ca and P as the major constituents in ABA with other constituents like Y, Ag, Nb, K, Al with some traces of Si whereas MK indicated Si and Al as major constituents with trace of Fe and other minor constituents element present include Ti, Nb, Y, Ag, Fe, Mg

and K, Cl and Ca. Obianyo *et al.* [40] revealed hydroxyapatite presence in ABA and Si presence in laterite led to improved cementitious properties of brick due to Ca and Si evident by ED X-ray analysis with higher strength.

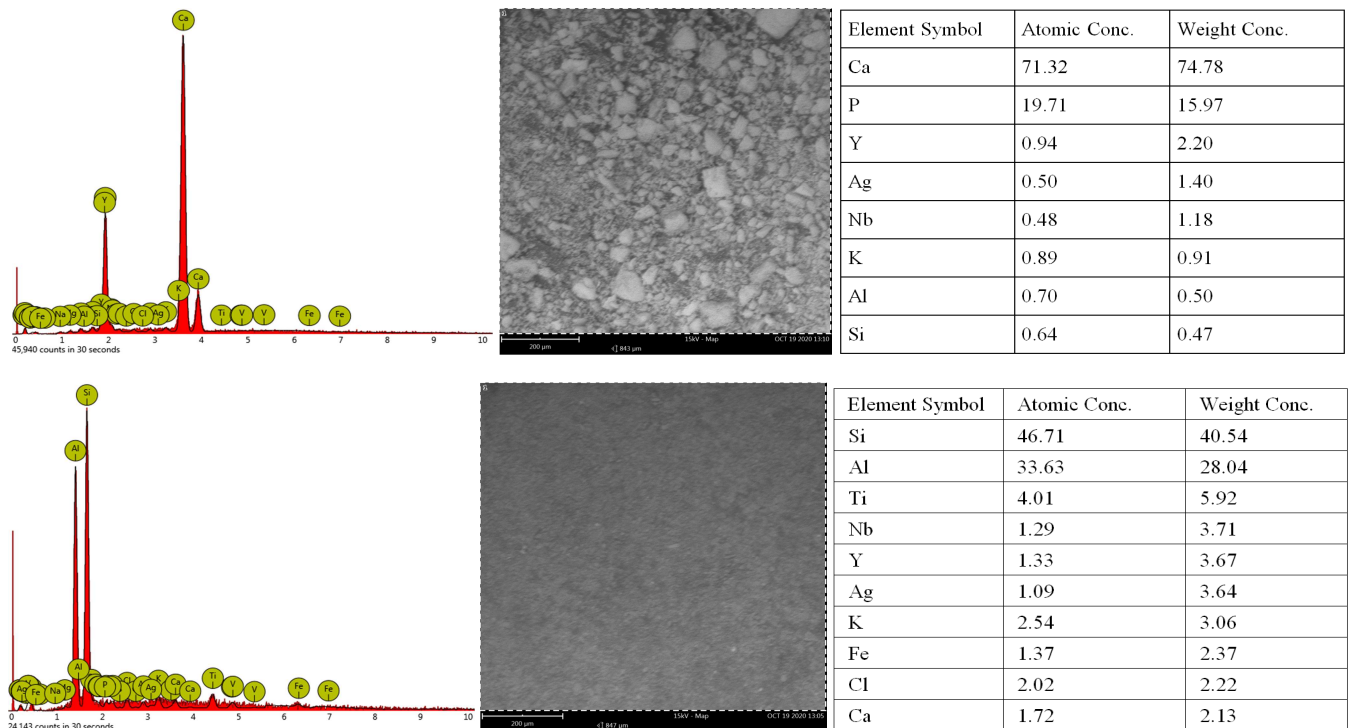


Figure 4. EDX analysis of (a) Animal bone ash (b) Metakaolin.

### 3.2. Standard Consistence of ABA-MK Cements

#### 3.2.1. Cement Replacement Effect on Consistence of ABA-MK Cement Blends

The physical properties of ABA-MK cement pastes and control pastes such as consistence, soundness and setting times are presented in Table 2. The water consistence of the various blended cements experienced an increase with increase in the cement replacement between 2.5 and 12.5 wt.% at various blending ratio between 0 – 1.0. Ternary cement blend with blending ratio, 0.2 and cement

replacement, 12.5 wt.% produced the highest consistence value of 35% (109.38% of PLC value) which could be linked with MK high fineness in comparison with PLC. The specific surface area and amorphous structure of MK were significantly higher than conventional cements employed according to El- Didamony *et al.* [36] and Dave *et al.* [41]. This finding agrees with Olubajo *et al.* [17], that the water consistence increased gradually with increase in the MK content between 5 to 25 wt.% cement replacement while RHA was held constant at 5 and 10 wt.% respectively.

**Table 2.** The Consistence, Setting times and Soundness of Cement Blends at various Mix Proportions.

S/No	Blends	ABA / ABA MK	Consistence (%)	Initial setting time (min)	Final setting time, (min)	Soundness (mm)
1	OPC	0.0	32.0	184	269	1.0
2	2.5MK	0.0	33.0	213	251	2.0
3	2MK0.5ABA	0.2	33.0	195	250	1.0
4	1.5MK1 ABA	0.4	33.0	190	231	1.0
5	1.25MK1.25 ABA	0.5	33.0	200	242	0.5
6	1MK1.5 ABA	0.6	32.0	174	224	0.0
7	0.5MK2 ABA	0.8	32.0	183	262	0.0
8	2.5 ABA	1.0	32.5	145	183	0.0
9	5MK	0.0	33.0	190	206	2.0
10	4MK1ABA	0.2	33.0	158	180	1.5
11	3MK2 ABA	0.4	32.0	154	199	1.0
12	2.5MK2.5 ABA	0.5	32.5	153	186	1.0
13	2MK3 ABA	0.6	33.0	163	186	1.0
14	1MK4 ABA	0.8	33.0	126	216	0.0
15	5 ABA	1.0	32.0	146	186	0.0
16	7.5MK	0.0	33.0	138	220	1.0
17	6MK1.5 ABA	0.2	33.0	134	192	2.0
18	4.5MK3 ABA	0.4	33.0	148	219	3.0
19	3.75MK3.75 ABA	0.5	34.0	166	233	2.0
20	3MK4.5 ABA	0.6	33.0	132	202	1.0
21	1.5MK6 ABA	0.8	32.0	126	201	1.5
22	7.5 ABA	1.0	32.5	126	140	0.0
23	10MK	0.0	35.0	176	246	2.0
24	8MK2 ABA	0.2	34.0	194	236	3.0
25	6MK4 ABA	0.4	32.5	151	203	2.0
26	5MK5 ABA	0.5	33.0	144	206	3.0
27	4MK6 ABA	0.6	33.0	151	221	3.0
28	2MK8 ABA	0.8	33.0	150	223	2.0
29	10 ABA	1.0	33.0	132	186	2.0
30	12.5MK	0.0	36.0	260	315	5.0
31	10MK2.5ABA	0.2	35.0	160	234	4.0
32	7.5MK5ABA	0.4	34.0	138	216	2.0
33	6.25MK6.25ABA	0.5	34.0	135	193	1.0
34	5MK7.5ABA	0.6	33.0	135	218	1.0
35	2.5MK10ABA	0.8	33.0	143	210	0.0
36	12.5ABA	1.0	32.5	152	214	0.0

**Table 3.** Mortar strength of various cement blends at various curing age.

%PLC	PLC	Blending ratio (ABA/ABA-MK ratio)	Mortar strength for various curing age N/mm <sup>2</sup>				
			3 days	7 days	28 days	60 days	90 days
100	100PLC	0.0	26.60	29.50	30.08	34.32	41.61
97.5	2.5MK	0.0	25.96	30.38	35.90	36.66	39.96
	2MK0.5ABA	0.2	24.52	26.64	29.78	33.79	38.18
	1.5MK1ABA	0.4	19.47	30.46	35.91	38.44	41.15
	1.25MK1.25ABA	0.5	25.43	32.42	36.88	41.13	48.73
	1MK1.5ABA	0.6	28.33	31.73	36.77	39.05	42.90
	0.5MK2ABA	0.8	23.52	29.15	32.00	40.12	43.65
	2.5ABA	1.0	25.50	29.32	32.27	36.00	45.08
95	5MK	0.0	21.58	30.77	32.53	38.14	44.78
	4MK1ABA	0.2	22.69	30.73	33.17	38.34	45.88



%PLC	PLC	Blending ratio (ABA/ABA-MK ratio)	Mortar strength for various curing age N/mm <sup>2</sup>				
			3 days	7 days	28 days	60 days	90 days
92.5	3MK2ABA	0.4	27.96	31.52	34.90	41.31	45.61
	2.5MK2.5ABA	0.5	24.58	27.38	34.18	36.05	40.01
	2MK3ABA	0.6	23.03	29.45	32.75	35.74	39.66
	1MK4ABA	0.8	23.15	25.81	30.47	32.28	35.01
	5ABA	1.0	25.98	28.71	33.05	39.00	47.44
	7.5MK	0.0	27.06	33.00	34.87	36.93	44.83
	6MK1.5ABA	0.2	25.61	27.00	35.96	38.89	39.96
	3MK4.5ABA	0.4	25.10	30.84	36.67	39.52	50.91
	3.75MK3.75ABA	0.5	21.37	31.81	35.50	40.70	45.13
	2MK5.5ABA	0.6	23.20	25.76	28.40	33.13	38.69
90	1.5MK6ABA	0.8	24.82	27.17	29.80	36.79	42.79
	7.5ABA	1.0	23.61	26.97	30.33	36.22	39.35
	10MK	0.0	23.94	27.94	30.24	33.35	39.22
	8MK2ABA	0.2	25.26	28.81	29.45	32.58	36.03
	6MK4ABA	0.4	24.85	27.11	30.46	31.63	36.88
	5MK5ABA	0.5	26.61	29.97	32.06	35.43	42.71
	4MK6ABA	0.6	23.56	28.07	32.16	37.32	45.68
	2MK8ABA	0.8	22.70	26.09	29.39	30.80	35.34
	10ABA	1.0	24.05	26.46	29.34	32.40	35.98
	12.5MK	0.0	24.22	30.29	32.95	35.67	39.08
87.5	10MK2.5ABA	0.2	24.00	27.05	32.24	34.12	41.61
	7.5MK5ABA	0.4	27.41	29.01	33.85	37.10	41.09
	6.25MK6.25ABA	0.5	24.73	26.20	32.14	34.68	42.38
	5MK7.5ABA	0.6	25.79	29.50	31.90	34.84	40.34
	2.5MK10ABA	0.8	22.95	26.03	30.27	33.27	36.05
	12.5ABA	1.0	23.83	26.58	28.88	31.32	36.44

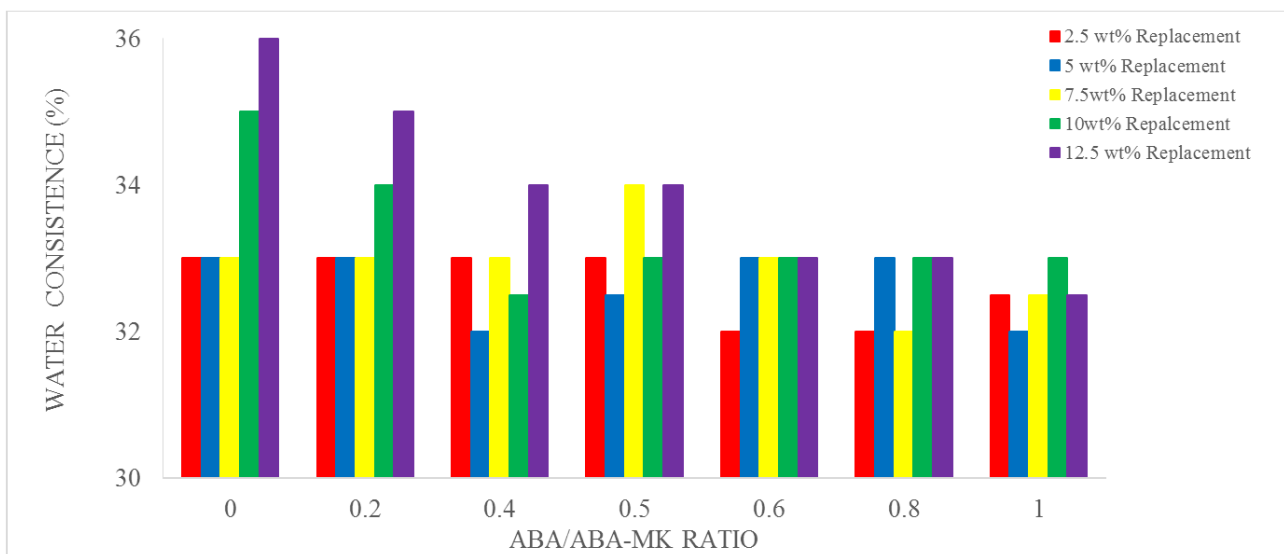


Figure 5. Effect of Blending ratio on the water consistence of various cement blends.

### 3.2.2. Effect of Blending Ratio on Water Consistence of ABA-MK Cements

Figure 5 shows the impact of blending ratio on water consistence of ABA-MK cements which was insignificant initially at lower blending ratio whereas at higher blending ratio increment resulted in a slight variation in the water consistence of ABA-MK cements. At higher cement replacements of 10 and 12.5 wt.% resulted in decrease in the water demand as the blending ratios was increased. This increase in the water consistence of ABA-MK cements may be a function of the quantity of MK content coupled with its reactivity owing to its enhanced specific surface area and

amorphous nature according to Brooks *et al.* [10] and similar trends was observed from Olubajo *et al.* [17] work on ternary cement blends containing MK and RHA.

### 3.3. Initial and Final Setting Times of ABA-MK-Cements

#### 3.3.1. Influence of Cement Replacement and Blending Ratio on Initial Setting Time of ABA-MK-Cements

Results indicated a diminution in the initial setting time as PLC was replaced with ABA and MK to produce ternary binder. An increase in the cement replacement from 2.5 – 12.5 wt.% with MK and ABA at a blending ratio of 0.5 resulted in a decrease in the initial setting time (acceleration) from 200 – 135 mins.

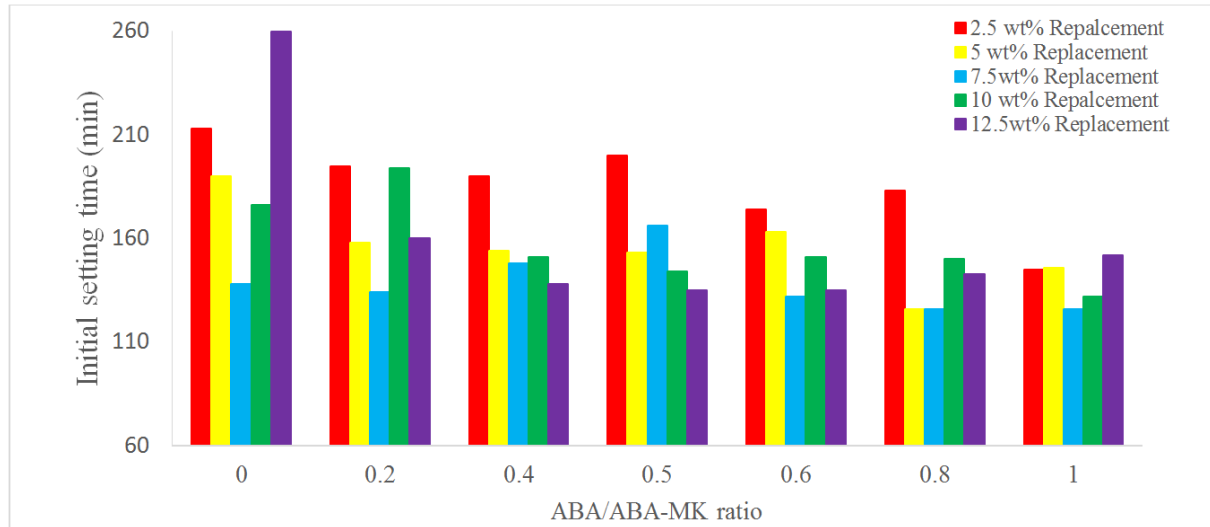


Figure 6. Blending ratio effect on the Initial Setting Time of ABA-MK-Cements.

Figure 6 illustrates the effect of blending ratio (MK-ABA) on initial setting time of ABA-MK cements. A decrease in the initial setting time was experienced from 213 – 145 mins when the blending ratio was increased from 0 – 1.0 at various cement replacement between 2.5 and 12.5 wt.%. This acceleration in the setting times could be due to amorphous nature of the silica present in MK along with its fineness. Thus, a contributory factor in the setting time acceleration owing to siliceous swift solubility in the MK, thereby, resulting in a faster pozzolanic

activity due to the fact that surface area, particle size, silicon oxide content and silica crystalline phase of the ash particle affect MK reactivity [17, 42, 43]. The production of calcium silicate hydrate (C-S-H) obtained from the high lime content of ABA reacting with silica in MK, resulting in accelerated setting time. The lime present in the cement matrix tends to shorten the setting of cements which agrees with Ipavec *et al.* [44] and Olubajo *et al.* [30, 45] due to provision of larger nucleation points facilitating hydration of cement.

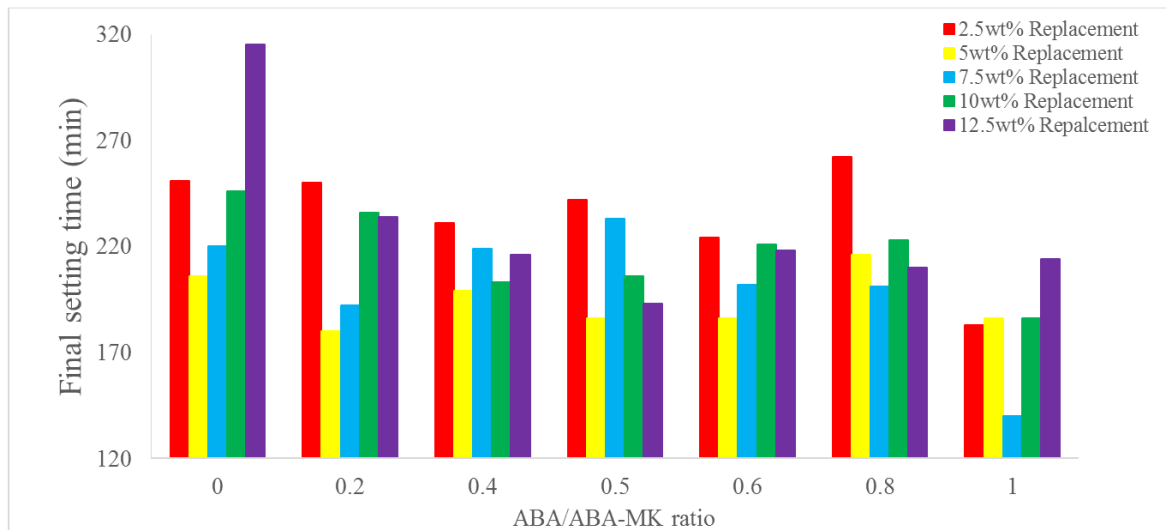


Figure 7. Effect of Blending Ratio on Final Setting Time of ABA-MK-Cements.

### 3.3.2. Influence of Cement Replacement and Blending Ratio on Final Setting Time of ABA-MK-Cements

The influence of blending ratio on the final setting time of ABA-MK cements was illustrated in Figure 7. The final setting time was shortened from 251 – 186 min at lower cement replacement of 2.5 wt.% as the blending ratio was increased except for blending ratio of 0.8 whereas at high cement replacement of 12.5 wt.%, the final setting time

diminished from 315 – 214 min as the blending ratio was increased. The reason for the accelerated final setting time is as a result of ABA inclusion which provide nucleation sites and accelerate the hydration reaction as the blending ratio was increased in comparison with MK cement blends. An increase the MK content (increase in cement replacement) at a given blending ratio resulted in the retardation of the final setting times. This retardation of setting time could be linked with clinker diminution, MK's high surface area/ reactivity,



hinderance of hydration by formation of  $\text{Mg}(\text{OH})_2$  and ettringite due to coating effect [10, 17, 36].

### 3.4. Soundness of MK-ABA-Cements

#### 3.4.1. Influence of Cement Replacement on Soundness of ABA-MK Cements

The influence of blending ratio and cement replacement on the volume expansion of ABA-MK cements were presented in Table 2. An increase in volume expansion (unsoundness) of blended cement was observed from 0.5 – 5 mm with increase in cement replacement from 2.5 – 12.5 wt.% at a given blending ratio. This significant increase in the volume expansion may be ascribed to lime's presence in the cement matrix which agrees Chatterji [46]. He suggested that free CaO and MgO available in the cement matrix is the sole

factor affecting the volume expansion and concluded that the expansion was due to the formation of hydroxides of magnesium and calcium.

#### 3.4.2. Influence of Blending Ratio on Soundness of ABA-MK Cements

Figure 8 indicated a step-by-step reduction in the volume expansion from 2.0 to 1.0 mm with an increase in the blending ratio from 0 – 1.0, at 2.5 wt.% replacement while the volume expansion experienced a decrease from 5.0 – 1.0 mm with an increase in cement replacement from 2.5 - 12.5 wt.%. This decrease in the volume expansion could be may be accredited to clinker diminution of clinker, available lime presence in the cement matrix possessing a significant lime content culminating in unsoundness of cement.

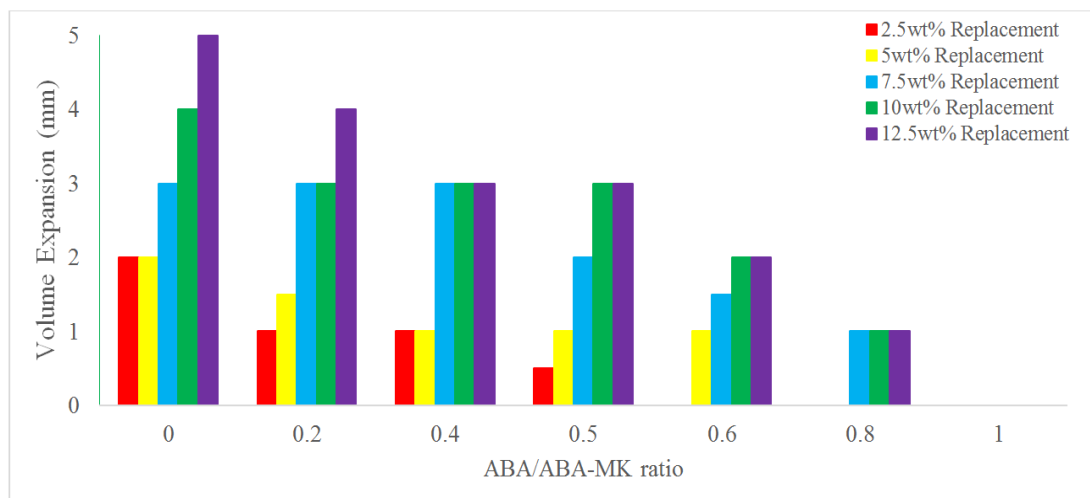


Figure 8. Effect of Blending Ratio of ABA and MK on Soundness of various cement blends.

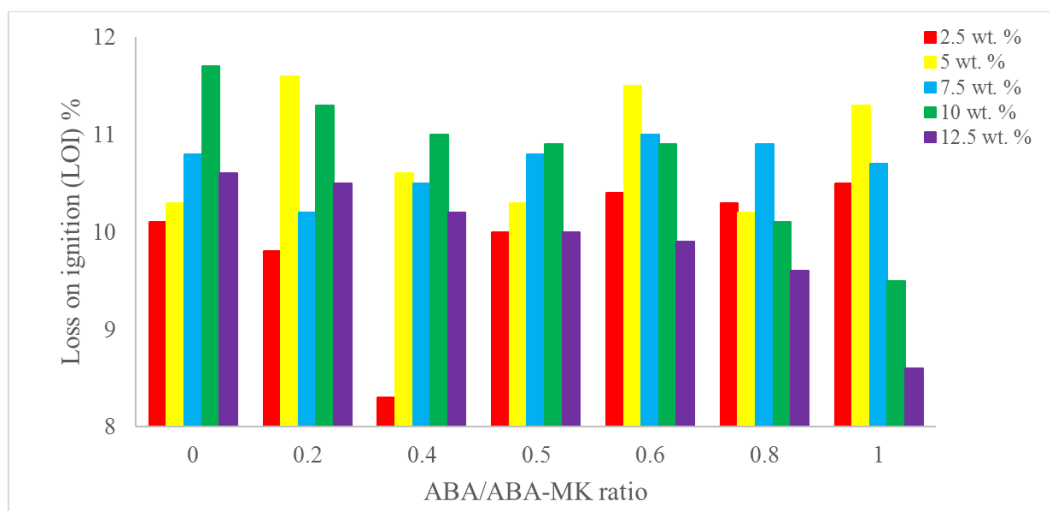


Figure 9. Effect of Blending ratio on the Loss on ignition of various ABA-MK cement blends.

### 3.5. Influence of Cement Replacement and Blending Ratio on the LOI of ABA-MK Cements

The influence of blending ratio and cement replacement on the LOI of ABA-MK cements was illustrated in Figure 9. An

increase in the LOI of the ABA-MK-cements were observed as the blending ratio was increased at lower cement replacement at 2.5 – 7.5 wt.%, whereas at higher cement replacement above 7.5 wt.%, as the blending ratio was increased (i.e., MK was gradually replaced with ABA) resulted in a decrease in the

LOI of the ABA-MK-cements. This reduction could be related to diminution of the clinker content which contributes greater losses on ignition with Portland limestone cement compared to ABA. An increase in the LOI of ABA-MK-cements was observed as the cement replacement was gradually increased for blending ratio 0 – 0.4 while for blending ratio between 0.6 – 1.0 resulted in a reduction in the LOI value, thus the LOI of MK is considered as the limiting factor and significantly influences the overall LOI.

### 3.6. Mortar Strength of MK-ABA Cements and Effect of Cement Replacement & Blending Ratio on Mortar Strength

The impact of blending ratio and cement replacement on the mortar strength at various curing ages of ABA-MK cements are presented in Table 3. A variation in the mortar strengths of ABA-MK cements were observed as the cement replacement was increased from 2.5 - 12.5 wt.% and as blending ratio was increased from 0 – 1.0 at a given cement replacement. For 3 days strength blending ratio of 0.6 and cement replacement of 2.5 wt.% produced the highest strength of 28.33 N/mm<sup>2</sup> (106.5% of control strength) while all these combinations (0.4, 5 wt.%, 0, 7.5 wt.%; 0.5, 10 wt.%; 0.4, 12.5 wt.%) produced better strength than control. The lowest compressive strength of 19.47 N/mm<sup>2</sup> (73.19% of control strength) was produced at cement replacement 2.5 wt.% and blending ratio 0.4. For 7 days strength blending ratio of 0.5 and cement replacement of 2.5 wt.% produced the highest strength of 32.42 N/mm<sup>2</sup> (109.90% of control strength) while the lowest compressive strength of 25.76 N/mm<sup>2</sup> (87.32% of control strength) was produced at blending ratio of 0.6 and cement replacement of 7.5 wt.%. Thus, the increase in the mortar strength of ABA-MK- cements could be linked with the calcite presence in ABA acting as a filler resulting in reduction in the porosity of the bulk cement matrix while MK presence produces additional C-S-H gel CAH from the remaining calcium hydroxide available in the cement matrix [14, 47]. Matschei [47] revealed

increment in early compressive strength of concrete blended with calcite and MK.

Figure 10 depicts how the 28 days strength of ABA-MK-cements are affected by blending ratio and cement replacement. The highest strength of 36.88 N/mm<sup>2</sup> (122.61% of control strength) was obtained for 28 days strength with blending ratio of 0.5 and cement replacement of 2.5 wt.% while the lowest compressive strength of 28.40 N/mm<sup>2</sup> (94.41% of control strength) was obtained at blending ratio of 0.6 and cement replacement of 7.5 wt.%. This improved mortar compressive strength observed was due to numerous nucleation sites being formed, leading to enhanced packing and higher reactivity which agrees with the findings of El-Diadamony *et al.* [36] and Olubajo *et al.* [30, 45, 48]. Results indicated from Table 3 that 80% of the ABA-MK-cements produced improved strength at 28 days in comparison with control. Mortar strength of ABA-MK cements for 60 days with blending ratio 0.4 and cement replacement 5 wt.% produced the highest strength of 41.31 N/mm<sup>2</sup> (120.37% of control strength) while the lowest compressive strength of 30.80 N/mm<sup>2</sup> (89.74% of control strength) was produced at blending ratio of 0.8 and cement replacement of 10 wt.%. Similarly results showed that at 74.28% of the cement blends produced better 60 days strength compared with control. This improved strength experienced at 28 and 60 days compared to control could be ascribed to pozzolanic reaction of reactive silica present in MK according to Olubajo *et al.* [17] between free lime from calcite in ABA. Mortar strength of ABA-MK cement for 90 days with blending ratio 0.4 and cement replacement 7.5 wt.% produced the highest strength of 50.91 N/mm<sup>2</sup> (122.35% of control strength) while the lowest compressive strength of 35.01 N/mm<sup>2</sup> (84.14% of control strength) was produced at blending ratio of 0.8 and cement replacement of 5 wt.%. Similarly results showed that at 51.42% of the cement blends produced better 90 days strength compared to control. The improved mortar strength of ABA-MK cement for curing age of 90 days could be due to formation of additional CSH via pozzolanic reaction coupled with dense packing due to filler effect [49].

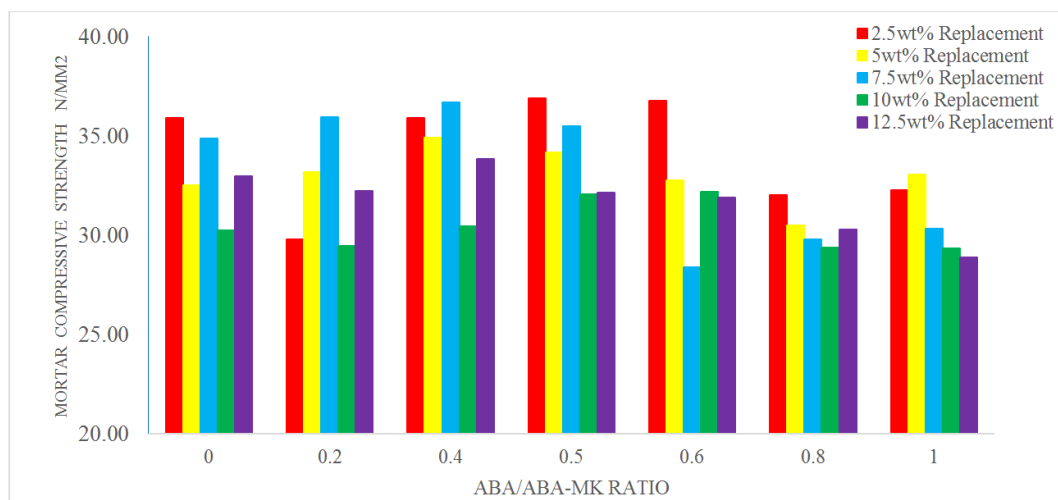


Figure 10. Effect of Blending ratio on the mortar strength for 28 days of various ABA-MK cements.

## 4. Conclusions

The following conclusions were outline based on observations and trends determined from the results.

- (1) Metakaolin is pozzolanic in nature and have the potentials to improve some specific properties of mortar. It was found that the oxide composition of major component of MK (sum of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  = 97.06%) higher than the minimum requirement of 70% of a good pozzolan according to ASTM C 618. ABA comprising mainly lime (53.86 wt.%) and Phosphate (40.96 wt.%) with high content of Hydroxylapatite as confirmed by Xray diffractometer. Although the oxide composition of ABA (the sum of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  less than 70%), but could be regarded as a cementitious filler/additive.
- (2) Blending ratio between 0 -1.0 has a limited influence on the water consistence of ABA-MK cements especially at lower replacement levels between 2.5 – 7.5 wt.% but at high replacement levels between 10 and 12.5 wt.% indicated a decrease in the water consistence within acceptable standards. This confirms the fact that cementitious materials possess minimal influence on the water consistency of ABA-MK-cements. The water consistence of ABA-MK-cements increases with increasing cement replacement owing to the narrow particle size distribution of MK and ABA resulting in high water requirement. The diminution of the clinker content and increased silica content (MK inclusion) are considered determinant for the value of water consistence of ABA-MK cements.
- (3) An increase in the blending ratio led to a decrease (acceleration) in both setting times of ABA-MK cements at various cement replacements. This acceleration in the setting times could be linked with the rapid solubility of the silica present in MK, thereby resulting in a quicker pozzolanic reaction due to the high lime present in ABA reacts to form calcium silicate hydrate. On the other hand, lime present tends to shorten cement setting time through formation of many nucleation sites thus, facilitating cement hydration rate. The cement replacement increases with decrease in the initial setting time of ABA-MK cements at various blending ratios while the final setting time experiences a retardation owing to clinker diminution coupled with the coating effect of hydrated ABA-MK cements with the ettringite formation.
- (4) Cement replacement increased with increase in volume expansion of ABA-MK-PLC blends at various blending ratios owing to the presence of increased  $\text{MgO}/\text{CaO}$  content due to inclusion of ABA and MK which are rich in lime. An increase in blending ratio gave rise to a stepwise reduction in the volume expansion at various replacement level due to the fact that PLC contains more free lime in comparison with ABA.
- (5) The LOI of ABA-MK cements experienced an increase with an increase in the cement replacement from 2.5 - 7.5 wt.% at various blending ratios whereas beyond 7.5 wt.% at blending ratios above 0.4 produced a reduction in the LOI of ABA-MK cements. The high LOI of MK compared to ABA was found to be responsible for the increase in the LOI of the ABA-MK-cements as the replacement level was increased. Cement replacement up to 7.5 wt.% produced an increase in the LOI of ABA-MK cements as the blending ratio was increased but beyond 7.5 wt.% resulted in a reduction in the LOI values. This reduction is due to the fact that ABA has a lower LOI value compared to MK, thus cement blends significantly replaced with ABA at high replacement experienced a decrease in its LOI values.
- (6) A slight decrease in the 28 days strength was experienced as the cement replacement with ABA and MK was increased at various blending ratios except for ABA/ABA-MK ratio = 0.2. This slight strength decrease could be linked with the pozzolanic activity which contributes to the strength gain despite the lower clinker content. The improved strength experienced by cement blended with ABA and MK despite clinker diminution could be linked with improved reactivity. A variation (series of increase/decrease and decrease /increase) in the strength was observed as the blending ratio was increased at a various replacement level. All ABA-MK cements strength increased progressively as the curing day were extended. This increment in strength was evident owing to pozzolanic activity coupled with increase in hydration rate as the cement blends are in contact with water.

## Conflict of Interest

The authors declare no conflict of interest.

## Acknowledgements

The authors acknowledging the support of Department of Civil Engineering, Department of Chemical Engineering of Abubakar Tafawa Balewa University, Bauchi Nigeria, Ashaka Cement Plc and Bua Cement Plc.

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