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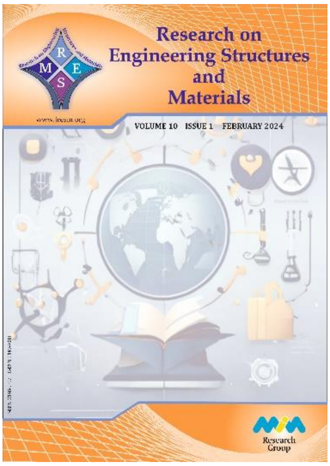

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Research Article

Impact of treatment temperature of metakaolin on strength and sulfate resistance of concrete

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Abstract

Calcined clay, a widely studied supplementary cementitious material, has shown positive impacts on concrete's microstructural properties, strength development, and durability. The variation in raw clay mineral concentration across different locations influences the optimal calcination temperature needed to activate its pozzolanic reactivity. This investigation focuses on studying the effects of calcination temperature on the characterization and pozzolanic reactivity of Nigerian Kaolinite clay. The clay was calcined at temperatures ranging from 600˚C to 900˚C for 2 hours. Characterization involved X-ray Diffraction (XRD), X-ray Fluorescence (XRF), and Scanning Electron Microscope (SEM) analyses. Blended mixtures, incorporating 10%, 20%, 30%, and 40% metakaolin as cement replacement, were assessed for workability, strength, and durability properties at 7, 14, 28, and 56 days to determine the clay's pozzolanic reactivity. XRF categorized the metakaolin as a class N pozzolan, while XRD indicated that 800˚C for 2 hours was necessary for complete dihydroxylation. Compressive, tensile, and sulfate resistance tests confirmed that treating the clay at 800˚C for 2 hours optimized its performance. The mix with 10% metakaolin outperformed the control by 6.4%, 14.7%, and 14.1% in compressive strength at 14th, 28th, and 56th days, respectively. While the best performance was at 10% replacement, levels up to 30% also demonstrated satisfactory results compared to the control, showing potential for achieving desired strengths. Linear regression models were also developed to establish the relationship between compressive and split tensile strengths across curing periods. The resulting equations demonstrate excellent predictive performance with correlation coefficients ranging from 0.928 to 0.991.

1. Introduction

All over the world, concrete is the most widely used construction material and its demand is expected to increase because of the rapid urbanization and infrastructural developments across the globe [1], [2]. Cement remains the most important composition in concrete as it is used as the binder but its production causes proliferation of CO_2 due to disintegration of limestone [3]. Cement accounts for up to 5% of the global anthropogenic CO_2 emission [4], [5]. CO_2 has been identified as one of the greenhouse gases and its reduction is required to reduce the impact of global warming. Besides, it requires large amount of heat energy (1450˚C) to produce cement from its clinker [5]. Therefore, the main concern of the industry is to reduce the carbon footprint, achieve cost efficient construction materials for a sustainable environment.

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Partial replacement of cement with supplementary cementitious materials (SCMs) from industrial by-products is another means of reducing consumption of ordinary Portland cement. Some of these SCMs are fly ash, silica fume, coffee silver skin, ground granulated blast furnace slag and agricultural wastes such as rice husk ash (RHA), and palm oil fuel ash. Utilization of SCMs enhanced strength and durability of concrete materials and this also serves as an indirect method of reducing CO_2 emissions in to the atmosphere [6]. The limited availability of most of the aforementioned SCMs in Nigeria due to the low level of industrialization hinders their application in concrete production in the country.

Materials such as calcined clays are also pozzolanic and requires lower energy input compared to cement [7]. Its availability in commercial quantities in most parts of the world also makes it preferred to other industrial by-product pozzolan. Internationally, many studies have investigated the use of calcined clay in concrete in the form of kaolinite, smectite, muscovite, illite and montmorillonite as a partial replacement for cement. They are reported to impact positively on the microstructure development, workability and strength properties, resistance to carbonation and chloride penetration, as well as reduced heat of hydration [6], [8], [9]. The kaolinite content of the calcined clay is the most important factor influencing the mechanical performance of calcined clay of the blended cement [8].

Kaolinite is one of the clay minerals that is found in claystone. Other clay minerals include illite, smectite, chlorite, vermiculite and montmorillonite. Kaolinite is a sheet silicate mineral formed by the alteration (chemical weathering) of rocks rich in feldspar through the process of hydrolysis [10]. A claystone with high percentage of kaolinite as the clay mineral is commonly termed kaolinite clay [11]. Kaolinite clay is found in large quantities in various parts of the country including Adamawa, Borno, Abia, Delta, Ekiti, Kaduna, Katsina, Kogi, Ogun, Ondo, Oyo, Plateau and Kwara State. The estimated kaolin mineral deposit reserve in the country is about 2 billion metric tons [12].

Metakaolin (MK) is a product of calcination (thermal treatment) of Kaolinite clay at a temperature range of 600 to 900°C [5], [13]. It is the amorphous alumino-silicate ($Al_2O_3.2SiO_2$) obtained when water is expelled from kaolinite clay ($Al_2Si_2O_5(HO)_2$) at high temperature [7], [14]. The process is known as dihydroxylation. The dihydroxylation process significantly influences the pozzolanic reactivity of the MK [7]. Various investigations have shown that the calcination temperature, heating duration and rate, cooling rate, and ambient conditions affect the composition and the reactivity of the resulting MK [13]. Studies such as those by Boakye et al. and others [15] have highlighted that the calcination temperature significantly impacts the pozzolanic activity index (PAI) of metakaolin. Calcination temperatures greater than 900°C often lead to increased crystallinity and reduced amorphous content, affecting the reactivity of metakaolin when blended with cementitious systems. Furthermore, investigations by Khaled et al. [16] emphasized that different calcination temperatures yield metakaolin with varying particle sizes and surface areas, influencing the pozzolanic reactivity and the microstructure of the resulting concrete. Research by Abiodun et al. [17] also indicated that metakaolin obtained at temperatures from 500°C to 800°C for 1hr duration exhibited enhanced mechanical properties in concrete, attributed to its amorphous phase content. In another study, Moodi et al. [14] investigated the effect of degree and duration of heating on the pozzolanic properties and reactivity of metakaolin obtained from Iranian kaolinite clay. The outcome of their study revealed that thermal treatment of 750°C to 850°C for 1hr was sufficient for the activation of the kaolin. It is worthy to emphasize that the concentration of the clay minerals as well as other impurities in a particular clay source varies for different locations as it depends on the parent rock and the degree of weathering. Therefore, the ideal temperature for calcination necessary to stimulate the pozzolanic reactivity within a specific clay source differs, contingent upon the mineralogical composition of the clay [13].

2. Research Significance

Despite the growing interest in supplementary cementitious materials (SCMs) for sustainable concrete production, a comprehensive exploration of the influence of treatment temperature on the performance of locally available kaolinite, especially in the context of Nigeria's construction industry, is not well addressed.

Nigeria, characterized by its rich reservoirs of kaolinite, presents a unique opportunity to investigate the practical viability of utilizing indigenous resources in concrete production. Despite this, the lack of comprehensive studies assessing the metamorphic effects of different calcination temperatures on Nigerian kaolinite and the subsequent performance of derived metakaolin in concrete production represents a gap in the current research landscape.

Addressing this gap is pivotal for several reasons. Firstly, it allows for a more profound understanding of the influence of indigenous metakaolin on concrete properties, encompassing its impact on workability, mechanical strength, durability, and resistance to environmental factors. Secondly, such investigation holds promise for developing tailored concrete mixtures that align with the specific climatic and environmental conditions prevalent in Nigeria, ensuring sustainable construction practices that resonate with the local context. Furthermore, a detailed exploration of locally sourced metakaolin offers a strategic pathway toward reducing dependency on imported SCMs, fostering economic sustainability within the construction sector. By providing empirical evidence on the feasibility and efficacy of utilizing Nigerian kaolinite-derived metakaolin, this research strives to offer pragmatic insights that could revolutionize concrete production practices in regions constrained by limited access to conventional SCMs.

Therefore, an in-depth investigation into the influence of treatment temperatures on Nigerian kaolinite, and subsequently, the performance of derived metakaolin in concrete formulations, stands as an indispensable step toward unlocking the full potential of indigenous materials in sustainable construction.

3. Materials and Methods

3.1 Materials

Cement: Portland limestone cement of grade 42.5 (Dangote 42.5R brand) obtained from a local supplier in Ilorin, Kwara state, Nigeria with its oxides composition and physical properties as presented in Table 1.

Aggregates: Naturally occurring river sand passing through BS sieve with aperture 2.36 mm was used as fine aggregates while coarse aggregates were angular-shaped granite chippings with maximum size of 12.5 mm. The granite chippings was purchased from a local vender while the sharp sand was sourced from Oyun River in Ilorin, Kwara State, Nigeria.

Kaolin: The kaolinite clay deposit was sourced from Lakiri village (Ogun State, Nigeria) located at latitude 7°19’25” N and longitude 3°28’44” E. The clay was first dried under natural atmospheric condition for some days and then grinded into powder and then sieved before being calcined at different temperature to produce metakaolin. Since there is no universally agreed optimal calcination temperature for metakaolin, the grinded clay samples were converted to metakaolin by applying heat treatment: Calcination at 600, 700, 800 and 900° C for 2 hrs. The resulting metakaolin samples passing through sieve BS 212-micron were characterized using X-Ray Fluorescence (XRF) spectrometer, X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis. This is necessary to determine the compounds, bond characteristics and morphology of the metakaolin, respectively.

3.2 Experimental Design and Mix Proportioning

In other to assess the impact of calcination temperature on the pozzolanic performance of metakaolin, a total of eight mixes, containing metakaolin prepared at different temperatures (600-900°C for 2 hrs), were investigated in this research as given in Table 1. The control mix was designed following the guideline given in COREN Concrete Mix design manual [18]. The percentage metakaolin varied as 10, 20, 30 and 40% in partial replacement of Portland Limestone Cement (PLC). Several tests were conducted on the fresh and hardened samples, and these include, setting time, workability, compressive strength, tensile strength, and sulfate resistance.

Table 1. Concrete Mix Design (kg/m^3)

S/N	Mix Code	Percent	CEM I	MK	F. A	C.A	SP (liter/100kg of cement)	w/c
1	0MK000	0	470	0	595	1100	--	0.5
2	10MK600	10	423	47	595	1100	--	0.5
3	10MK700	10	423	47	595	1100	--	0.5
4	10MK800	10	423	47	595	1100	--	0.5
5	10MK900	10	423	47	595	1100	--	0.5
6	20MK800	20	376	94	595	1100	--	0.5
7	30MK800	30	329	141	595	1100	1.5	0.5
8	40MK800	40	282	188	595	1100	1.5	0.5

3.3 Test Methods

3.3.1 Characterization Tests

The elemental composition in oxide form, phase transition and morphological characteristics of the calcined clay samples were determined using XRF, XRD and SEM analyses. The chemical compositions of the representative samples of the calcined clay were obtained using thermo Scientific ARL QUANT'X EDXRF Spectrometer at Umaru Musa Yar'adua University, Katsina. The output of XRF along with the provision of ASTM C618-17a [19], was used to determine either particles of Metakaolin are pozzolanic or not. X-Ray diffraction (XRD) measurements were carried out on randomly selected powdered samples of calcined clay using an Empyrean diffractometer with a cupper anode material at the laboratory of the Nigeria Geological Survey Agency in Zaria, Kaduna state, Nigeria. The goniometer which forms the central part of the Empyrean diffraction system has a radius of 240 mm. The sample was analyzed using a 2-theta angle range of 5-80 deg C with a step of 0.026261 at 30 seconds per step. The morphology of the calcined clay samples was analyzed by SEM using a JOEL-JSM 7600F analyzer at the Rolab research and diagnostic laboratory, Ibadan, Nigeria.

3.3.2 Fresh Property Tests

The normal consistency test was measured on a vicat apparatus in line with ASTM C187-98 [20]. The initial and final setting times of the blended cement paste samples were also measured according to ASTM C403/C403M-16 [21]. The workability properties of the concrete mixes adopted in the study as reported in Table 1 were also determined through slump test as per BS 12350-2 [22].

3.3.3 Hardened Properties Tests

The compressive strength of each of the concrete mix codes were tested on 100 mm cube specimens after 7, 14, 28 and 56 days using a compression testing machine with load rate of 0.9 kN/s capacity. The cube preparation and compressive strength testing followed the procedure given in BS EN 12390-3 [23]. The freshly prepared concrete samples were filled up in three layers and each layer received 25 equally distributed strokes in the moulds. The concrete samples were demolded after 24 hours of casting and cured in water for 7, 14, 28 and 56 days before crushing. The reported compressive strengths were the average of three tested specimens at various curing days.

The tensile strength was tested on a cylindrical specimen of 100 mm diameter by 200 mm height as per the provision of BS EN 12390-6 [24]. The cylindrical moulds were filled with freshly prepared concrete samples in three layers with each layer receiving 25 equally distributed strokes. The samples were demolded after 24hrs and cured for 7, 14, 28 and 56-days prior to determination of the split tensile strength. The reported tensile strengths also represent the average of three tested specimens at various curing days.

3.3.4 Sulfate Resistance

Some concrete structures, such as storage tanks and wastewater sewers for industrial effluents, are exposed to aggressive environments including sulfuric acid solution. Degradation of concrete material occurs as it is exposed to such severe condition. The sulfate ions in the sulfuric acid solution react with portlandite to produce gypsum. The produced gypsum reacts with calcium aluminate hydrate to produce ettringite. The by-product, ettringite causes expansion of the concrete which eventually affects its strength. In this study, the resistance of the concrete mix to sulfate attack was determined in term of strength loss when the sample was cured in 5mol/dm^3 of sulfuric acid solution for 7, 14, 28 and 56 days respectively.

4. Results and Discussion

4.1 Effect of Treatment Temperature on The Characterization of Metakaolin

4.1.1Effect of Treatment Temperature on Chemical Composition of Metakaolin

The effect of calcination temperature on the chemical composition of the calcined clay samples, as determined by X-ray Fluorescence (XRF) analysis, is presented in Table 2. Metakaolin (MK), an aluminosilicate material, undergoes dehydroxylation during calcination, resulting in an increased Si/Al ratio and Al/OH ratios in the samples compared to those present in the kaolinite group $[Si_4]Al_4O_{10}(OH)_8.4H_2O$. Additionally, the thermally treated clay, as depicted in Table 2, contains traces of ferric oxide (Fe_2O_3) and magnesia (MgO), suggesting the presence of illite and smectite, albeit in minimal quantities.

Table 3 shows oxide compositions in the MK such that the SiO_2+Al_2O_3+Fe_2O_3 should not be < 70% while Sulfur trioxide (SO_3) is limited to 4% maximum, such that it can be classified as a class N pozzolan according to ASTM C618 [19]. The moisture content (mc) percentage is also limited to 3%. The results in Table 3 show that all the calcined clay samples meet the requirements for the oxides compositions of class N pozzolan. Based on these criteria, only MK700, MK800 and MK900 samples satisfied the requirements of class N pozzolan according to ASTM C618 [19] specification.

Table 2. Oxides composition and physical properties of the materials

	CEM I*	MK600	MK700	MK800	MK900	FA	CA
Al_2O_3	5.35	41.26	41.14	45.00	46.23		
SiO_2	20.62	35.41	35.86	37.14	38.32		
Fe_2O_3	3.07	0.56	0.57	0.55	0.57		
CaO	61.79	0.03	0.03	0.02	0.02		
MgO	1.93	3.00	3.01	3.35	4.12		
K_2O		0.12	0.13	0.1	0.1		
TiO_2	0.12	1.62	1.64	1.74	1.78		
MnO	0.06	0.01	0.01	0.01	0.01		
SO_3		0.13	0.09	0.11	0.08		
P_2O_5		0.16	0.13	0.15	0.14		
Specific gravity	2.83	2.29	2.14	2.11	2.04	2.44	2.03
Water absorption (%)	-	-	-		-	2.92%	0.40%
Fineness Modulus	-	-	-		-	2.2	2.65
Moisture Content %	-	6.5	2.36	2.56	1.42		
Fineness (%)	0.79%	-	-	-	-	-	

Salman et al. [1]*

Table 3. Comparison of oxides to composition

Sample	$SiO_2+Al_2O_3 + Fe_2O_3$ (%)	SO_3 (%)	MC (%)
MK600	77.23	0.13	6.5
MK700	77.57	0.09	2.56
MK800	82.69	0.11	2.36
MK900	85.12	0.08	1.42
ASTM C618	≥ 70	≤ 4	≤ 3

4.1.2 Effect of Heat Treatment on Phases of Metakaolin

The calcination temperature (600°C, 700°C, 800°C, and 900°C) influences the phase transition of the calcined clay samples, as can be seen in Fig. 1. At 600°C calcination temperature, noticeable peaks include that of Kaolinite (K) and Quartz (Q). Calcining kaolinite before or at temperature of 600°C, the kaolin clay present in clay has not undergone complete transformation. Quartz is a crystal mineral of silica oxides abundantly available in the earth's surface. At 700°C, the noticeable peaks include that of Kaolinite (K) and Anatase (A). Incomplete transformation of kaolin clay could only be the reason where kaolinite minerals could still be present in the calcined clay. The anatase is a crystalline mineral of titanium oxides and one of the major impurities found in kaolin clay [1]. Majority of the kaolinite and other materials present in the clay calcined at 600°C and 700°C calcination temperatures had been transformed to amorphous materials at the 800°C as indicated by the presence of fewer anatase peaks and presence of humps at points between when 2thetha is 20° and 30°. At 900°C, the only noticeable peaks here are that of anatase which are known for its titanium oxides origin. Several peaks of Kaolinite (K), Anatase (S) and Quartz (Q) shown in clay calcined at 600 and 700°C show that calcined clay at 600 and 700°C are majorly in crystal forms. Little broad humps noticed at 600 and 700°C may demonstrate presence of fewer amorphous materials. Presence of broad humps at between when 2thetha is at between 20° and 30° in the diffractograms at calcination temperature of 800 and 900°C indicated the amorphousness of the materials. Peaks represented anatase shown presence of crystal materials at both phases. As shown in Fig. 1, clay calcined at 800°C has fewer anatase peaks in comparison to calcined clay at 900°C. The broad areas in calcined clay at 800°C is slightly bigger compared to that of 900°C, all of these indicated the degree of amorphousness in 800°C as compared to that 900°C. Presence of many anatase peaks in clay calcined at 900°C could be a sign indicating beginning of transformation from amorphous materials to crystal materials [25], [26].

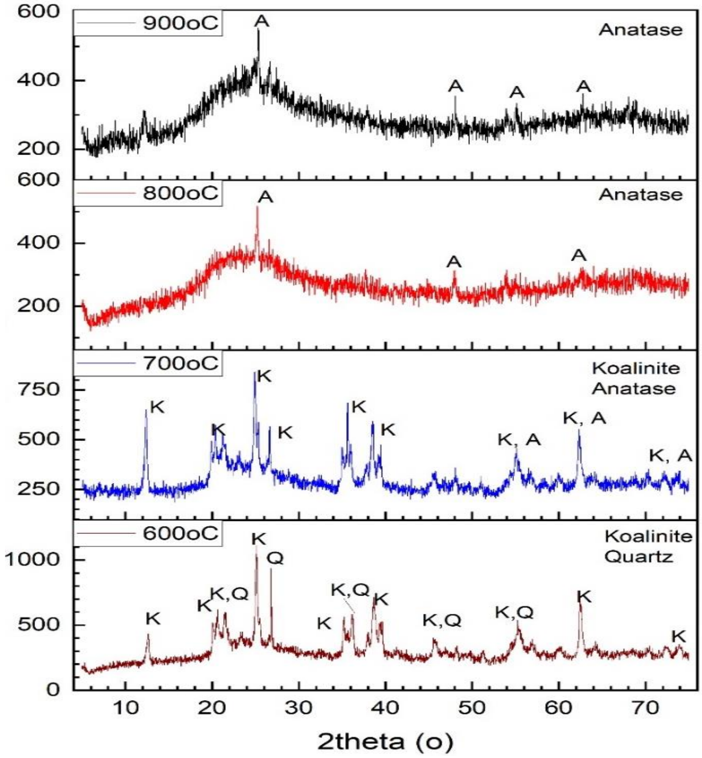


Fig. 1. XRD of the metakaolin at different calcination temperature

4.1.3 *Effect of Heat Treatment on the Microstructural Properties of Metakaolin*

Kaolinite consists of alternating plate of silica and alumina connected by a strong bond. The micrographs of the calcined clay samples are presented in Fig. 2. At calcination temperature of 600°C, the calcined clay materials that are produced are closely packed together with some forms of voids indicating presence of microspores. They are arranged in regular pattern and their shape are majorly spherical. Also noticeable in calcined clay formed at 600°C are particles of different sizes indicating incomplete calcination of kaolin particles. At 700°C, the calcined clay formed are of different shapes; while some are irregular cuboid, others are flaky, and long cylindrical shapes. There are also noticeable micropores in the SEM micrographs of calcined clay formed at 700°C. Calcined clay formed at 800°C have regular shapes with regularly arranged and packed particles. The noticeable micropores are smaller as compared to micropores found in calcined clay produced at the calcination temperature of 600 and 700°C. The arrangement of calcined clay formed at 900°C shows that the particles are not arranged in regular pattern, sizes and shape seems to be different greatly. The particles appeared at point as if they are cob wires and are in layers. The presence of micropores all around calcined clay particles. This may be a sign of transformation to crystalline particles.

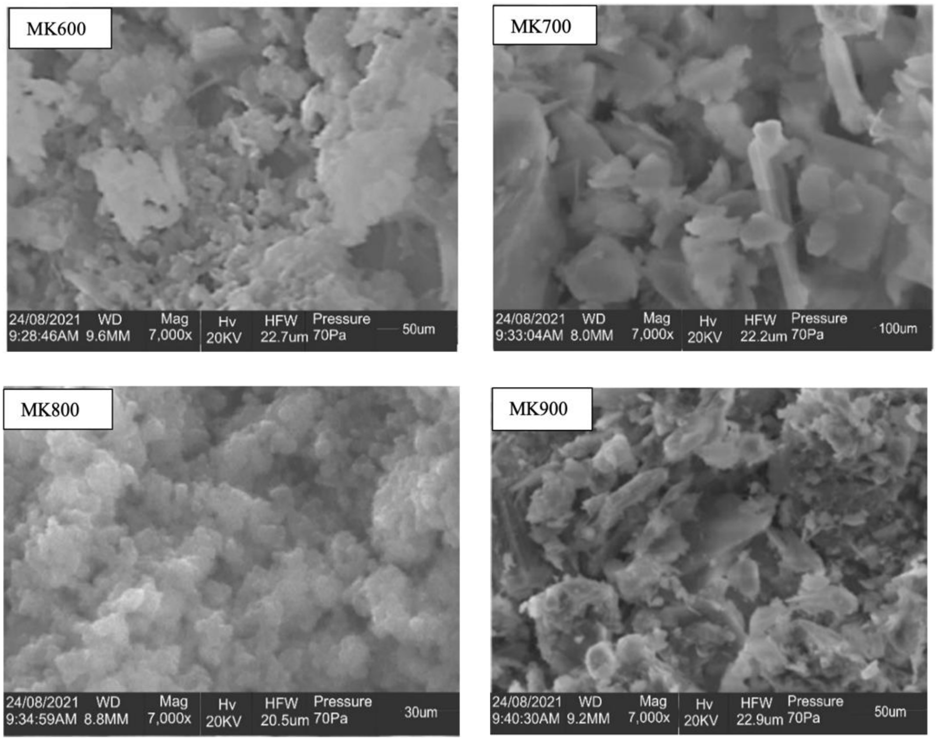


Fig. 2. SEM image of the metakaolin produced at different calcination

4.2 Effect of Metakaolin on Fresh Properties of Concrete

4.2.1 Initial and Final Setting Time

Table 4 presents the findings regarding the initial and final setting time of the cement paste blended with MK. The results revealed that replacement of cement with 10% metakaolin reduced both the final and initial setting time compared to the control group irrespective of the treatment temperature. Although, it was also observed that the setting time increased with increment in the treatment temperatures. This can be attributed to MK's ability to decrease the fluidity of cement, resulting in a reduction in free water content. As the setting time of cement primarily depends on the water-to-cement ratio, the addition of MK to the cement paste could effectively reduce the setting time. Similar observations have been reported by Khamchin et al. [27].

Contrarily, a study by Li et al. [28] reported that incorporating 5% to 20% metakaolin in cement increased both the final and initial setting time. It is important to mention that Li et al. (2022) used varying dosages of superplasticizer in their mix designs, which were proportional to the quantities of MK. It is widely known that superplasticizers can influence the setting time of cement paste and concrete [29].

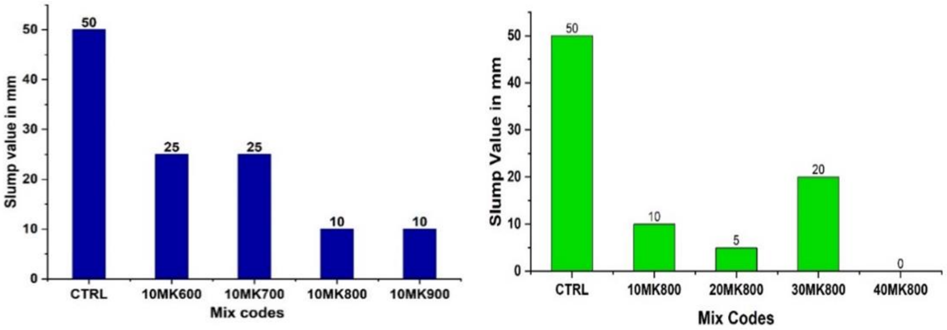
Moreover, as the percentage of MK replacement increased, the final and initial setting times of the cement paste also increased. This can be attributed to the fact that higher amounts of MK required more water to achieve the standard consistency of the cement paste. Consequently, the increased water-to-cement ratio delayed the rate of cement setting, resulting in a longer setting time. Thus, beyond a 20% replacement (specifically at 30% and 40%), the setting time of the cement paste exceeded that of the control, as indicated in Table 4.

Table 4. Initial and final setting time results

Setting time (mins)	CEM I	10MK600	10MK700	10Mk800	10MK900	20MK800	30MK800	40MK800
Initial	103	77	83	88	94	97	103	109
Final	349	309	316	323	332	348	351	358

4.2.2 Workability of Concrete

The impact of metakaolin on the slump values of mixtures is illustrated in Fig. 3. The findings demonstrate that the workability of concrete mixtures is adversely affected by the inclusion of metakaolin. Fig. 3a reveals that as the treatment temperature of metakaolin increased from 600°C to 900°C, the slump values of the concrete mixtures decreased. The flow characteristics of concrete are significantly influenced by the morphological features of metakaolin, including its size, shape, and surface area. The SEM image of MK600 in Fig. 2 reveals particles that could hinder the flow of the concrete mixture, potentially impacting its flowability. Moreover, the presence of flaky and elongated cylindrical particles in the sample treated at 700°C (Fig. 2) might further restrict flow and adversely affect the concrete's workability. The SEM micrographs also highlight the substantial surface area of well-arranged and densely packed MK800 particles, influencing water demand and the pace of pozzolanic reactions in the concrete mix. These increased surface areas offer more reactive sites for chemical interactions with calcium hydroxide, enhancing strength and durability. Nonetheless, it is important to note that excessively high surface areas can increase water demand and reduce workability due to heightened water absorption by the metakaolin particles.



(a)

(b)

Fig. 3. Effect metakaolin on slump values

The effect of high-volume replacements is depicted in Fig. 3b. The results indicate that increasing the percentage replacement from 10% to 40% at 10% intervals significantly decreases the slump flow and, consequently, the workability of the concrete. Among the mixes, the one containing 30% metakaolin treated at 800°C achieved a slump value of 20 mm, which is slightly higher than the other mixtures. It is important to note that this particular mix included superplasticizer, thus the improved workability can be attributed to the addition of superplasticizer. On the other hand, the mix incorporating 40% metakaolin as a cement replacement recorded zero slump. This further confirms that calcined clay has an adverse effect on concrete workability. Similar observations have been reported by Salau and Osemeke [30] and Salman et al. [1].

4.3 Effect of Metakaolin on the Strength Properties of Concrete

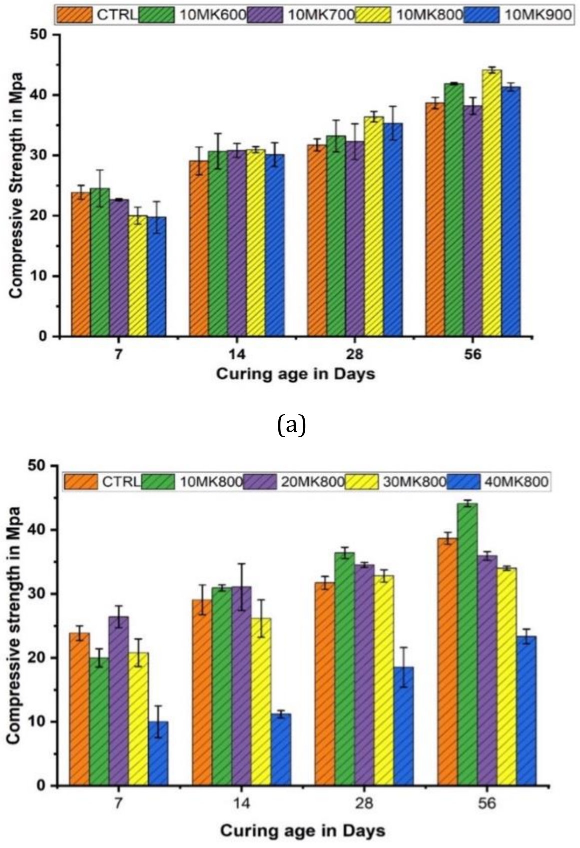
4.3.1 Compressive Strength

The effect of partial replacement of cement with metakaolin (MK) obtained at different treatment temperatures on the compressive strength of concrete is depicted in Fig. 4. The results presented in Fig. 4a indicate that the inclusion of 10% MK by weight of cement reduced the 7-day strength of the concrete, except for samples containing MK obtained at 600˚C, which exhibited a strength greater than that of the control by 2.7%. The reduction in early-age strength could be linked to several factors. As a pozzolanic material, its slower reaction compared to cement during early hydration stages delays strength development. Moreover, the particles of metakaolin fill spaces between cement grains, potentially altering the water-to-cementitious material ratio and causing a dilution effect that impacts early strength. Additionally, while metakaolin reacts with calcium hydroxide to form C-S-H gel, crucial for long-term strength, this process might not sufficiently compensate for reduced early strength due to its slower activation during the initial stages of concrete setting and curing. These combined effects contribute to the observed reduction in early strength when metakaolin is used as a replacement for cement.

At the 14th day, all samples containing 10% MK exhibited compressive strength slightly exceeding that of the control, regardless of the calcination temperature. This suggests a faster rate of strength development in samples containing 10% MK between 7 and 14 days. The strength gain continued beyond the 28-day of curing, signifying the significant influence of the later-age pozzolanic effect of MK. The best performance in terms of 28-day and 56-day compressive strength was recorded in concrete samples containing 10% MK obtained at 800˚C for 2 hours. The compressive strength of the mix (10MK800) was higher than that of the control by 14.72% and 14.12% at 28 days and 56 days, respectively. The observed increase in strength at 28 days and 56 days, resulting from the partial replacement of cement with metakaolin, could be attributed to several factors. The results of XRF presented in Table 3 and XRD depicted in Fig. 1 confirm the pozzolanic nature of metakaolin, hence its gradual reaction extending beyond the initial stages of concrete formation. This prolonged pozzolanic activity continually forms additional calcium silicate hydrate (C-S-H) gel, a key factor enhancing concrete strength over time. Furthermore, this pozzolanic activity enhances the formation of finer, more reactive particles, contributing to a denser and more homogeneous concrete microstructure, ultimately bolstering long-term strength. Additionally, the interaction between metakaolin and the cementitious matrix, notably in the presence of calcium hydroxide from cement hydration, generates a synergistic effect. This interaction further amplifies the formation of C-S-H gel, strengthening the concrete during the extended curing period. These intricate interactions, derived from metakaolin's pozzolanic properties and its significant influence on the concrete's microstructure and prolonged curing, collectively explain the observed increase in strength observed at 28 days and 56 days when metakaolin replaces cement in concrete formulations.

To examine the impact of higher volume replacement of cement with MK on concrete strength properties, samples containing 20%, 30%, and 40% of MK calcined at 800˚C

(MK800) were tested at 7, 14, 28, and 56 days of curing, as reported in Fig. 4b. The mixes containing 10%, 30%, and 40% of MK800 exhibited lower strengths compared to the control at the 7-day curing period. Although the samples containing 20% MK800 showed strength higher than that of the control at 7 days, this result does not align with the other findings and is therefore considered an outlier. At the 14-day of curing, samples containing 10% and 20% MK800 exhibited compressive strength higher than the control by 6.4% and 6.9%, respectively, while mixes incorporating 30% and 40% MK800 exhibited lower strength than the control, with 40MK800 recording the lowest strength. At the 28-day of curing, only samples from the 40MK800 mix exhibited strength lower than the control by 41.6%, whereas the specimens from 10MK800, 20MK800, and 30MK800 mixes achieved strengths greater than the control by 14.71%, 8.82%, and 3.3%, respectively. At the 56-day mark, however, only the 10MK800 mixes showed an improvement in strength of 14.11% compared to the control. Consequently, it can be concluded that a 10% replacement of cement with MK demonstrated optimal performance in terms of 14-day, 28-day, and 56-day compressive strength. This aligns with the conclusions of Busari et al. [11] and Tawfiq et al. [31]. However, mixes containing up to 20% and 30% MK800 could still achieve 108.80% and 103.4% of the designed strength at 28 days and, 93% and 88% of the control strength at 56 days, respectively. Therefore, a replacement level of up to 30% may still be adopted to achieve the desired design strength but with adequate quality control checks.



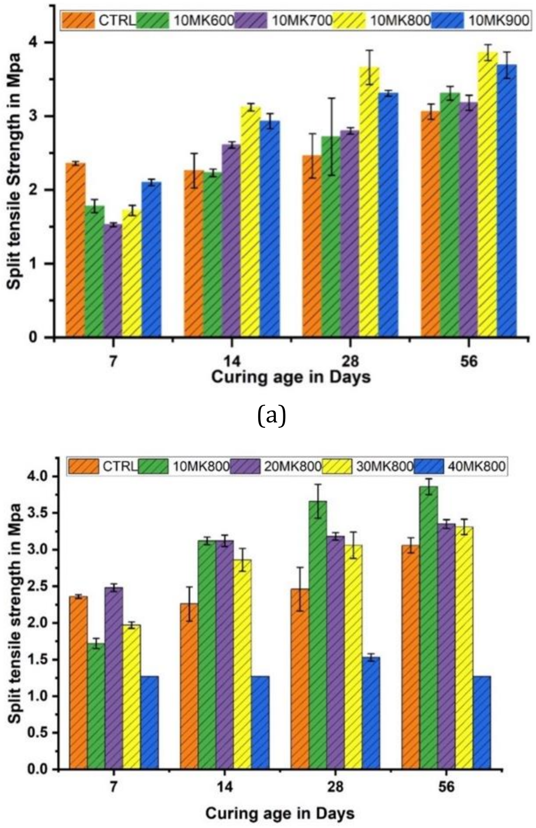
(a)

(b)

Fig. 4. Compressive strength of concrete containing metakaolin

4.3.2 Split Tensile Strength

Split tensile test is an indirect method of measuring tensile strength of concrete. The split tensile strength of the samples measured at 7, 14, 28 and 56-days is shown in Fig. 5. As expected, the result followed similar trend with that of compressive strength since the tensile strength is dependent on the compressive strength [32]. As shown in Fig. 5a, blending of cement with 10% MK negatively influenced the 7th day split tensile strength. The reduction in strength also increased with increase in calcination temperature. At 14th, 28th and 56th day, the tensile strengths of specimens incorporating 10% MK generally exceed that of the control irrespective of the calcination temperature with the calcined clay obtained at 800˚C for 2hrs giving the best performance. The impact of higher volume replacements is indicated in Fig. 5b. Replacement of cement with 10%, 20% and 30% metakaolin led to increment in split tensile strength by 38.05%, 38.05% and 26.54% respectively at 14th day; 48.78%, 29.27%, and 24.34% respectively at 28th day; 26.14%, 9.45% and 8.17% respectively at 56-day. Just as in the case of compressive strength, the samples containing 20% MK800 showed strength higher than that of the control at 7 days, this result does not align with the other findings and is therefore considered an outlier. Although replacement of cement with 10% metakaolin gave the best performance as per split tensile strength for all the curing days, replacement level of up 30 % still outperformed the control after 56 days of curing.



(a)

(b)

Fig. 5. Split tensile strength of concrete containing metakaolin

4.4 Correlation Matrix

The correlation coefficient, a statistical indicator measuring the linear relationship between variables, was utilized in this study. Specifically, the relationship between the strength attributes of blended mixes integrating metakaolin treated at varied temperatures (ranging from 600 to 900˚C for 2 hours) and control samples were evaluated. Tables 5A and 5B show results indicating strong positive correlations between the control samples and blended mixes. Notably, within the blended concrete mixtures, samples containing metakaolin calcined at 800˚C exhibited the highest correlation values, reaching approximately 95% for compressive strength and 60% for split tensile strength, respectively. This is in line with Guilford's rule of thumb with the following statistical ranges r<20%, 20%<r<40%, 40%<r<70%, 70%<r<90%, and r>90%, corresponding to an almost negligible correlation, low correlation, moderate correlation, high correlation, and very high correlation, respectively [33], [34].

Table 5a. Correlations matrix for compressive strength

		CTRL	10MK600	10MK700	10MK800	10MK900
CTRL	r	1				
	p-value					
10MK600	r	0.853**	1			
	p-value	0.000				
10MK700	r	0.907**	0.896**	1		
	p-value	0.000	0.000			
10MK800	r	**0.949****	0.855**	0.887**	1	
	p-value	**0.000**	0.000	0.000		
100MK900	r	0.904**	0.779**	0.873**	0.891**	1
	p-value	0.000	0.003	0.000	0.000	

**. Correlation is significant at the 0.05 level.

Table 5b. Correlations matrix for tensile strength

		CTRL	10MK600	10MK700	10MK800	10MK900
CTRL	r	1				
	p-value					
10MK600	r	0.504	1			
	p-value	0.094				
10MK700	r	0.525	0.813**	1		
	p-value	0.080	0.001			
10MK800	r	**0.593**	0.759**	0.978**	1	
	p-value	**0.006**	0.004	0.000		
10MK900	r	0.562	0.865**	0.969**	0.954**	1
	p-value	0.057	0.000	0.000	0.000	

**. Correlation is significant at the 0.05 level (2-tailed)

Thus, further investigation was conducted using the linear regression model (LRM) to establish the correlation between the compressive strength of concrete samples—incorporating varied percentages (0, 10, 20, 30, and 40%) of metakaolin obtained at an optimum temperature of 800˚C—and their corresponding split tensile strength for each of the curing periods: 7 days, 14 days, 28 days, and 56 days. This follows that using this set of equations, either of the two parameters can be predicted if the other parameter is available. Four different linear equations were modeled; one per curing period. There were fifteen (15) samples per curing period, and these were divided into two parts. Part A consists of ten (10) data while Part B consists of the remaining five (5) data. Parts A and B were used for model development and model validation respectively. The results of the model development and validation are shown in Tables 6-8.

As shown in Table 2, the R^2 values at the different curing periods range from 53% to 77%. This R^2 value shows how the independent variables were able to explain the dependent variables.

Table 6. Regression statistics

Parameter/Curing Periods	7days	14days	28days	56days
Multiple R	0.88	0.73	0.87	0.87
R^2	0.77	0.53	0.75	0.76
Adj. R^2	0.74	0.47	0.72	0.73
S.E. (n=10)	2.84	4.84	3.27	3.13

The p-values in all four cases, as seen in table 7, show that the independent variable (split tensile strength) is a good predictor of the dependent variable (compressive strength) as these values are less than 0.05 at a confidence interval of 95%. The null hypothesis is, therefore, rejected. Thus, the resulting linear simple regression equations are expressed in Equations 1-4.

Table 7. Linear regression model parameters

Variables		Coefficients	*SE*	*P-value*
f_{cu4}	c_4	13.52	4.64	
	f_{t4}	7.18	1.41	0.0009
f_{cu3}	c_3	9.85	4.65	
	f_{t3}	7.67	1.56	0.0012
f_{cu2}	c_2	7.16	6.82	
	f_{t2}	7.42	2.47	0.0170
f_{cu1}	c_1	-0.85	4.14	
	f_{t1}	10.84	2.08	0.0008

Model validation was done by using Equations 1-4 to predict the compressive strengths (f_{cu}) at 7 days, 14 days, 28 days, and 56 days curing periods respectively using their corresponding split tensile strength (f_t) values. The performances of these equations were evaluated by computing the Mean Errors (MEs) [33], [34], Correlation coefficient (r), Coefficient of Determination (r^2) [35], and Nash Sutcliff Efficiency (NSE) [34] using Equations 5-8, respectively. The results are presented in Table 8.

$$f_{cu1} = -0.85 + 10.84f_{t1} \tag{1}$$

$$f_{cu2} = 7.16 + 7.42f_{t2} \tag{2}$$

$$f_{cu3} = 9.85 + 7.67f_{t3} \tag{3}$$

$$f_{cu4} = 13.52 + 7.18f_{t4} \tag{4}$$

$$ME = \frac{Exp.Value - \ Modeled\ Value}{Exp.Value} * 100 \tag{5}$$

$$r^2 = \left(\frac{\sum_{i=1}^{n} (Exp.Value - \overline{Modeled\ Value}) * (Modeled\ Value - \overline{Modeled\ Value})}{\sqrt{\sum_{i=1}^{n} (Exp.Value - \overline{Exp.Value})^2 * (Modeled\ Value - \overline{Modeled\ Value})^2}} \right)^2 \qquad (6)$$

$$r = \left(\frac{\sum_{i=1}^{n} (Exp.Value - \overline{Modeled\ Value}) * (Modeled\ Value - \overline{Modeled\ Value})}{\sqrt{\sum_{i=1}^{n} (Exp.Value - \overline{Exp.Value})^2 * (Modeled\ Value - \overline{Modeled\ Value})^2}} \right) \qquad (7)$$

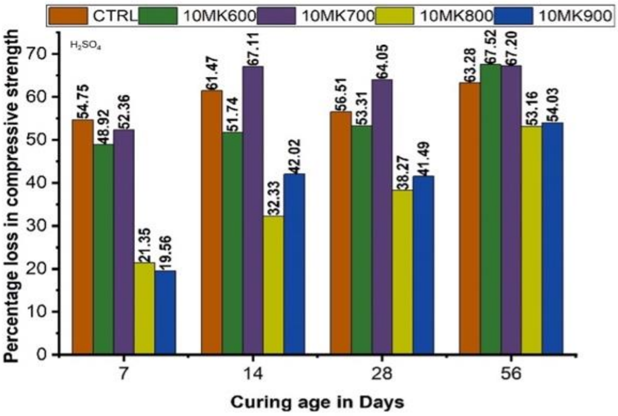
$$NSE = 1 - \left(\frac{[(\sum_{i=1}^{n} (Exp.Value - Modeled\ Value)^2]}{[\sum_{i=1}^{n} (Exp.Value - \overline{Exp.Value})^2]} \right) \qquad (8)$$

Table 8. Model Performance Evaluation Results

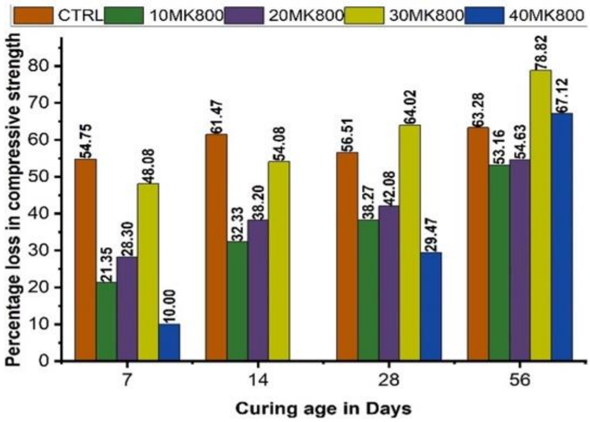
fcu	Equations	A.M.E.	Corr. (r)	r^2	N.S.E.	Remark
f_{cu1}	$-0.85 + 10.84f_{t1}$	0.07	0.991	0.981	0.912	Excellent
f_{cu2}	$7.16 + 7.42f_{t2}$	0.15	0.967	0.935	0.798	Excellent
f_{cu3}	$9.85 + 7.67f_{t3}$	0.04	0.928	0.861	0.851	Excellent
f_{cu4}	$13.52 + 7.18f_{t4}$	-0.03	0.961	0.923	0.903	Excellent

4.5 Effect of Metakaolin on Resistance to Sulfuric Acid Attack

Fig. 6 shows the result of strength loss in the samples at various curing days. From Fig. 6a, it is clear that 10MK800 and 10MK900 mixes exhibited better resistance to strength loss across all the curing ages when compared to the control although 10MK800 performs better at 14, 28 and 56-days. This agrees with the report of Khatib et al. [7]. The percentage loss in strength was also observed to increases with the curing days. Fig. 6b shows that increasing the MK800 beyond 20% reduces the effectives of the concrete mix against acid attack after 56-days of curing. This further validates the previously presented XRD result, which showed that best pozzolanic property is obtained when the kaolinite clay is exposed to heat treatment for 2 hours. Other studies including the work of [3, 5, 36] have also reported that inclusion of MK in concrete mix alters the acid resistance property. Masood et al. [37] linked the improved durability performance to reduction in the portlandite produced in the blended mix since it contains lower quantity of cement.



(a)



(b)

Fig. 6. Percentage strength loss in concrete containing MK when cured in H_2SO_4

It was also opined that MK particles could react with free portlandite in pozzolanic reaction to produce more C-S-H. Furthermore, Metakaolin's pozzolanic reaction leads to a denser concrete microstructure by filling voids and refining the pore structure. This densification reduces the pathways for sulfuric acid penetration, thereby minimizing the concrete's susceptibility to acid attack.

5. Conclusions

From the results of the experimental analysis on the impact of calcination temperature on pozzolanic reactivity of metakaolin conducted in this research, the followings are concluded:

- Blending of cement with 10 to 20 % of metakaolin reduced both the initial and final setting time of cement paste when compared to the control. Beyond 20% replacement, however, the setting time of the cement paste was higher than that of the control.
- The inclusion of metakaolin in the concrete mix negatively impacted its workability, regardless of the treatment temperature. This decline in workability could be attributed to the fine particle size and large surface area of the metakaolin particles leading to an increased water demand.
- This decline in workability could be attributed to the improved pozzolanic reaction within the concrete mix, resulting from the large surface area of metakaolin particles and subsequently leading to an increased water demand.
- The partial replacement of cement with metakaolin negatively impacted the 7th-day strength of concrete due to a delayed pozzolanic reaction of metakaolin, as a result of the dilution effect of metakaolin on cement.
- The mix incorporating 10% metakaolin as replacement for cement outperformed the control mix by 6.4%, 14.7% and 14.11% as per 14th, 28th and 56th day compressive strength respectively. However, mixes containing 20% and 30% metakaolin are still favorable, achieving 108.80% and 103.4% of the control strength at 28days, and 93% and 88% of the control strength at 56days respectively. Metakaolin reacts with calcium hydroxide formed in cement hydration, producing extra cementitious compounds such as calcium silicate hydrate (C-S-H) gel, which later enhances the overall strength of the concrete.

- Also, the optimum performance as per 14, 28 and 56 days split tensile strength was recorded in samples incorporating 10 % metakaolin thermal treated at 800 °C for 2 hrs. The tensile strength was improved by 38.0 %, 48.7 % and 26.1 % at 14th, 28th and 56th day respectively. However, it is worthy to note that mix containing 20% and 30% are still desirable as per tensile strength since they achieve strength higher than the control at after 14, 28 and 56 days of curing.
- With regards to resistance to acid attack, blending of cement with up to 20% metakaolin obtained at 800° C for 2 hrs showed better resistance to acid attack across all the curing ages when compared to the control and other mixes. This is due to the fact that metakaolin's pozzolanic reaction leads to a denser concrete microstructure by filling voids thereby reduces the pathways for sulfuric acid penetration.
- The correlation analysis also indicated strong positive associations between the compressive and tensile strength properties of concrete incorporating metakaolin. Specifically, the mix containing metakaolin treated at 800°C demonstrated the highest correlation, reaching 95% for compressive strength and 60% for split tensile strength.
- Based on these results, the optimum calcination temperature for the clay source considered in this study is 800°C for 2 hrs. The optimum performance in term of compressive strength, tensile strength and durability properties was recorded at 10% replacement, although replacement level of up to 30% could still be utilized to achieve the desired strength.

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