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Parametric Study of Matisaa Gray Rock as a Potential Clinker Material

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Authors' contributions

This work was carried out in collaboration with all authors. Author MG conceptualized the idea, designed the study, performed the experiments and data analysis, wrote the protocol and the first draft of the manuscript. Author MI conceptualized the idea, interpreted the data, reviewed and edited the first draft and supervised the work. Author Otieno Fredrick conceptualized the idea, interpreted the data, reviewed and edited the first draft, and supervised the work. All the authors read and approved the final manuscript.

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ABSTRACT

This study aimed at evaluating Matisaa gray rock (MGR) for clinker production. MGR is naturally abundant in Matisaa, a rural area in Mwingi West District, Kitui county, Kenya. It is locally used as a gabion filler and other concrete structures with desirable physico-mechanical properties. This research employed a controlled experimental design to determine the clinker qualification of MGR. This was based on particle size analysis and raw meal moduli. The standard sieve tests and a Blaine meter were used in the determination of particle size while the raw meal moduli were determined from the respective cement oxides in MGR, which were determined using wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. It was observed that 69.65% of the particle size composition of MGR was less than 90 μm. Out of this composition, 71.60% of the particle sizes were less than 45 μm, contributing to a specific surface area of 292.5 m^2kg^{-1}. The hydraulic modulus (2.05 – 2.61) and lime saturation factor (0.87 – 0.98) are quite desirable though the silica and alumina ratios are higher than the standard range due to the low proportions of Fe_2O_3 and Al_2O_3

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content. The sulfatisation modulus is also undesirable due to the high content of SO_3. Thus, without beneficiation, Matisaa gray rock would lead to the production of low-quality clinker. However, the general parametric comparison of Matisaa gray rock with Konza shows that it has the potential for utilization as a clinker raw material.

Keywords: Matisaa gray rock; Konza kunkur; raw meal moduli; clinker.

1. INTRODUCTION

The cement industry is currently seeking alternative raw materials to produce clinker due to high depletion rates of the existing ones [1]. In Kenya, most clinker raw materials are sourced from the coastal areas around the Indian ocean. These raw materials have been greatly depleted leaving the cement industry with a bleak future if the situation is not arrested [2]. In recent years, some organically based potential materials such as bagasse ash and rice husk ash have been dedicated to this study but with little assurance of sustainability. It is therefore important to have a variety of more reliable alternatives. MGR is found in a terrestrial location in Mwingi West District, Kitui county, Kenya. Its physical appearance suggests it is a sedimentary type of rock. MGR is locally used by Matisaa residents as a gabion filler. This application among other physical attributes presents promising properties that need scientific investigation. One of the physical properties investigated in this study is the particle size distribution. This represents a key parameter of any clinker raw material. The particle size distribution is because of the component's grinding efficiency. If the mineralogical composition of cement remains constant, then its strength class is governed mainly by the particle size distribution [3]. Particle size reduction of most cementitious materials is an energy-intensive process. The energy consumption during grinding is directly related to the time taken to grind material to the desired particle sizes [4]. Additionally, the compressive strength and curing properties of cement are reliant upon its particle size distribution. Small particle sizes have a large surface area that enhances the compressive strength and curing qualities of cement. It has been established that a higher compressive strength requires wide particle size distribution whereas a faster hydration rate requires narrow particle size distribution [5]. Particles that are smaller than 2 μm cause cracking of cement by setting exothermically whereas those larger than 75 μm can never hydrate completely [6]. Early hydration of cement is enhanced by cementitious materials through the provision of nucleation sites for the precipitation of hydration products [7].

The raw meal moduli of clinker are essential in governing the clinker kiln conditions [8]. Clinkerization process should be geared towards producing quality clinker using less energy. The quality of clinker raw materials is governed by its combustibility and sintering ability in the kiln [9]. This can be predetermined by calculating the raw meal moduli once the chemical composition of the raw materials is established. The said chemical composition is based on the fundamental oxides of cement and their proportions (wt.%) have a major impact on the clinker quality [9, 10]. These fundamental oxides are CaO, SiO_2 Fe_2O_3, Al_2O_3, MgO, SO_3, Na_2O, and K_2O [11]. Raw meal moduli refer to the relations between the oxides of cement and are defined by five parameters; the hydraulic modulus (*HM*), lime saturation factor (*LSF*), silica ratio (*SR*), alumina ratio (*AR*), and the sulfatisation modulus (*SM*). These moduli are given by Equations 1 – 6 [12].

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \quad (1)$$

$$LSF = \frac{CaO + 0.75MgO}{(2.80)SiO_2 + (1.20)Al_2O_3 + (0.65)Fe_2O_3} \quad (2)$$

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (3)$$

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad (4)$$

$$SM = \frac{SO_3}{(1.292)Na_2O + (0.850)K_2O} \quad (5)$$

If the MgO value is higher than 2 wt.%, Equation 2 is rendered inappropriate for the determination of *LSF*. This is because any excess MgO tends to be present as free periclase mineral after calcination, thus giving the incorrect values of

LSF [12]. However, the British Standard -12, provides an alternative formula for determining the LSF of clinker materials containing than 2 wt.%, MgO , as given in Equation 6 [13].

$$LSF = \frac{CaO - 0.7SO_3}{(2.80)SiO_2 + (1.20)Al_2O_3 + (0.65)Fe_2O_3} \quad (6)$$

In addition to clinker quality, these equations also provide a 'virtual burnability test' regarding free lime which a major compromiser to the quality of clinker. However, from a practical perspective, successful clinker is produced by evaluating the effect of particle size distribution by measuring free lime at different specified temperatures [14,15].

2. MATERIALS AND METHODS

2.1 Design of Experiment

The study utilized a controlled design for the parametric study of MGR as a potential clinker material. Konza kunkur which is an established clinker raw material used by East African Portland Cement Company Ltd. (EAPCC), Athi River, Kenya, was the control sample. These tests were done in East African Portland Cement Company Ltd. (EAPCC), Athi River, Kenya.

2.2 Sample Preparation

The original sample of Matisaa gray rock was in the form of a stone and its conversion into compressed powder involved several steps. Matisaa gray rock was cleaned in a sonicator for 30 minutes at room temperature to remove any surface contaminants. The rock is porous and therefore it was dried in an oven at 105°C for 24 hours to obtain a standard dry weight according to ANSI/ASTM R97- 47 [16]. It was then crushed into manageable sizes (10 – 20 mm) then pulverized using a Herzog pulverizing machine. The sample was then ground using a ball mill for 30 minutes to produce average grain sizes of the micron size. To ensure that the grain size was of micron range the sample was passed through a 1 mm sieve. Only the particles that passed through the sieve were used for further work. Fig. 1 shows the initial sample and its appearance after each subsequent preparation step.

2.3 Sample Characterization

2.3.1 Particle size distribution

The particle size distribution for milled samples was carried out on 90 µm and 45 µm -sieves, respectively to obtain two samples, one of < 90 other of < 45 µm by following the ASTM C618 - 12a method [17]. For < 90 µm particle size evaluation, 50.000 g of the sifted MGR dust were put into a 90 µm-sieve and gradually agitated for five minutes to freely pass through the sieve mesh. The mass of the particles that passed was recorded and further sieved through the 45 µm-sieve. Due to the fineness level of particles <45 µm, wet sieve evaluation was carried out for the < 45 µm , where the complete passage of the sample was aided by applying a controlled stream of distilled water over the sieve. The wet mass of the sample was recorded and dried in an oven at 105°C for 24 hours to attain a constant mass. The constant mass was recorded as the new mass of the sample. A similar parallel procedure was applied to Konza kunkur.

2.3.2 Specific surface area

For the specific surface area (SSA), Matisaa gray rock sample was run and compared to that Konza kunkur in the Blaine Analyzer (CM/L 0278348). The Blaine test was carried out by loading the samples (uncompressed powders) in the sample compartment. The samples were tightly mounted on the top of a U-tubed manometer which was filled partially with dibutyl phthalate (Blaine fluid). The time taken for the dibutyl phthalate to drop to the set position of the manometer column was measured. The measured time was then used to compute the specific surface area of the sample, S in comparison to the reference material, S_s as governed by Equation 7. The procedure was repeated two more times for validation of the results consistency.

$$S = S_s\sqrt{T/T_s} \quad (7)$$

Where T is the flow time of the material sample, and T_s is the flow time of the reference material.

2.3.3 Raw meal moduli

The raw meal moduli of Matisaa gray rock and Konza kunkur was calculated from their respective oxide compositions. These oxides were determined using wavelength dispersive X-ray fluorescence spectrometer, WDXRF (PANalytical AXIOS). Based on Equations 1 – 6, and the respective cement oxide proportions obtained, the raw meal moduli for MGR and Konza kunkur were determined.

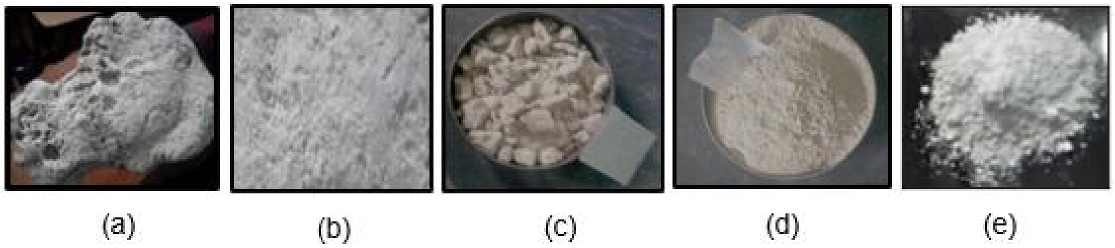

Fig. 1. Schematic representation of the sample preparation steps: (a) As-collected sample, (b) Cleaned rock, (c) Crushed to sizes of 10 – 20 mm, (d) Pulverizing to the size of 1 mm, (e) Sifted dust of micron-size particles

3. RESULTS AND DISCUSSION

3.1 Particle Size Distribution

Particle size distribution is a key parameter that defines the percentage of the desired particles after grinding a mass of a solid. The time taken to grind a given solid to a certain size is proportional to the energy intensiveness of the solid. Using this criterion, the energy intensiveness of MGR was compared with that of Konza kunkur by evaluating the proportion of the particles that were smaller than 90 and 45 µm. The results obtained are represented in Fig. 2.

It was observed that 69.65% of the particle size composition of Matisaa gray rock was less than 90 µm. Out of this composition, 71.60% of the particle sizes were less than 45 µm. On the other hand, Konza kunkur was composed of 60.0% < 90 µm-sized particles with a 69.65% composition of < 45 µm-sized particles. The particle size distribution of MGR was comparable to that of Konza kunkur as depicted in Fig. 2. According to the ASTM C618 - 05 [18] standard, for proper hydration kinetics of natural pozzolans to occur, 66% of the particles should be 45 µm-sized. MGR meets this requirement thus indicating a potential for proper hydration kinetics of the resultant product.

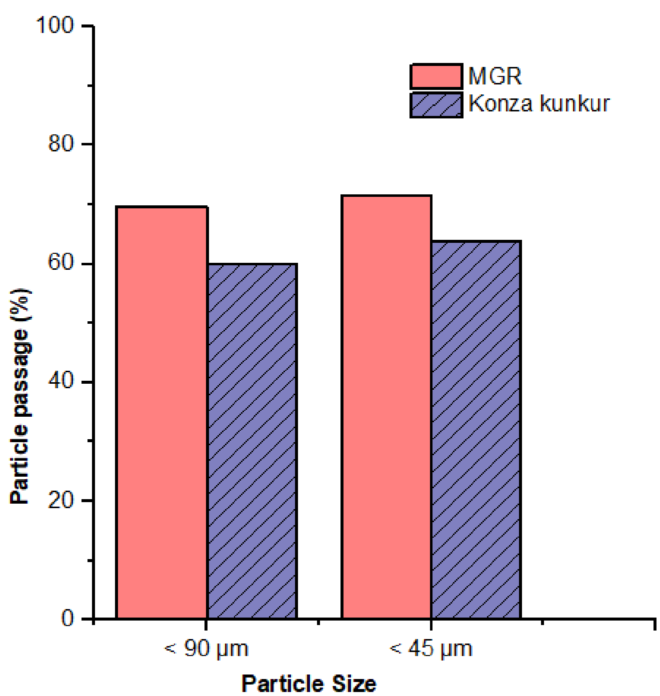

Fig. 2. A comparative bar graph of particle passage analysis of Matisaa gray rock against Konza kunkur. MGR stands for Matisaa gray rock

3.2 Specific Surface Area

Specific surface area (SSA) is the total surface area of a material per unit of mass, and it varies inversely as the particle size. SSA is the property that enables solids' interaction with the ambiance. This study discusses the SSA of Matisaa gray rock in comparison to that of Konza kunkur and typical SSA of other established cementitious materials. The comparison of MGR with Konza kunkur is shown in Fig. 3.

The SSA of MGR and Konza kunkur were observed to be 292.5 m^2kg^{-1} and 298.3 m^2kg^{-1} respectively. These observations show that both Matisaa gray rock and Konza kunkur require a comparable amount of energy to attain the same specific surface area. Goncharenko and Bondarenko argue that the specific surface area for many raw materials of cement range between 250 – 450 m^2kg^{-1} [19]. The SSA of MGR falls within this range making it a potential cement material.

3.3 Raw Meal Moduli

The measured raw meal moduli of MGR is discussed in comparison to the acceptable limits for each modulus (Hydraulic modulus (*HM*), lime saturation factor (*LSF*), silica ratio (*SR*), alumina ratio (*AR*), and the sulfatisation modulus (*SM*)). These moduli were calculated from the respective cement oxides of MGR and Konza kunkur shown in Table 1.

As shown in Table 1, the fundamental oxides of cement in Konza kunkur were also found in MGR except SO_3 , Na_2O , and K_2O . Among these oxides, the average proportions of CaO , SiO_2 , and MgO are comparable within a reasonable error margin while those of Fe_2O_3 and Al_2O_3 vary significantly. The effect of these variations is evident on the corresponding raw meal moduli as shown in Table 2.

The *HM* of Matisaa gray rock ranges from 2.05 – 2.61. This *HM* value is comparable to that of raw Konza Kunkur (1.86 – 1.94) and also lies within the recommended limits (1.7 $\leq$ *HM* $\leq$ 2.3 [20]). The *HM* range Matisaa gray rock indicates that is energy efficient, free from free lime, and therefore would produce clinker of good quality.

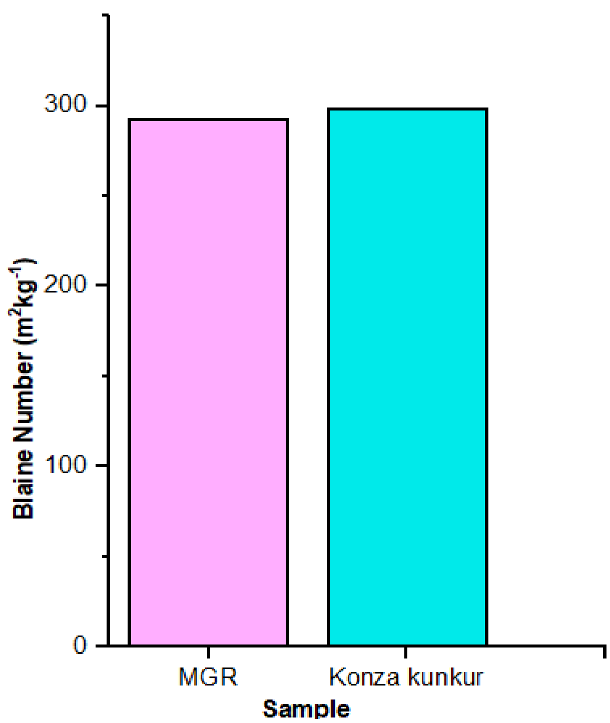

Fig. 3. A comparative bar graph of Blaine numbers of Matisaa gray rock against Konza kunkur. MGR stands for Matisaa gray rock

Table 1. Cement oxides (wt.%) in Matisaa gray rock and Konza kunkur

Oxide	Matisaa gray rock	Konza kunkur
CaO	39.03 – 46.42	34.43 – 47.46
SiO_2	13.92 – 16.79	14.93 – 17.13
Fe_2O_3	0.47 – 4.81	2.93 – 4.98
Al_2O_3	0.55 – 1.04	0.66 – 2.24
MgO	1.56 – 3.56	1.49 – 3.35
SO_3	3.30 – 6.06	-
Na_2O	0.11 – 0.21	-
K_2O	0.59 – 2.64	-

Cement oxides of Matisaa gray rock and Konza kunkur

Table 2. Raw meal moduli of Matisaa gray rock and Konza kunkur

Raw Material	*HM*	*LSF*	*SR*	*AR*	*SM*
Matisaa gray rock	2.05– 2.61	0.82 – 0.92	2.87 – 13.65	0.85 – 4.63	1.69 – 3.87
Konza kunkur	1.86 – 1.94	0.77 – 0.88	2.37 – 4.16	2.22 – 4.44	0.0

Cement oxide ratios of Matisaa gray rock and Konza kunkur

The average MgO proportions for MGR and Konza kunkur are 2.56 and 2.42 wt.% respectively. Having MgO values that are higher than 2.0 wt.%, Equation 6 was used to calculate the *LSF* for MGR and Konza kunkur. The respective LSF ranges obtained are 0.82 – 0.92 and 0.77 – 0.88 for MGR and Konza kunkur. The recommended range of *LSF* is 0.80 – 0.98 [14], which fits in that of Matisaa gray rock. This indicates that clinker from Matisaa gray rock would be easy to burn and thus energy-efficient, form complete alite and belite phases and does not contain free lime which hampers the burnability of the raw meal. LSF values higher than 0.98 imparts harder burning and thus higher fuel consumption and tends to produce unsound cement [21].

The silica ratio of Matisaa gray rock ranges from 2.87 – 13.65. This *SR* value is far beyond the acceptable limits ($1.5 \leq SR \leq 3.2$.). It indicates that Matisaa gray rock would form high calcium silicates and less aluminate and ferrite (solid/liquid phase). This is due to the low content of Fe_2O_3 and Al_2O_3 in Matisaa gray rock. This high *SR* value indicates that clinker from Matisaa gray rock would form by harder burning of the raw meal and thus higher energy consumption. Such high SR values also hint at the possible deterioration of the kiln lining [21], thereby necessitating the beneficiation of Matisaa gray rock for clinker production.

The AR value predicates the potential relative content of aluminate and ferrite phases in the resultant clinker [22]. The alumina ratio of Matisaa gray rock (0.85 – 4.63) is beyond the acceptable limits ($1.5 \leq AR \leq 2.0$). This could be due to the unproportionate content of Fe_2O_3 and Al_2O_3 in Matisaa gray rock. *AR* values higher than 2.0 tend to increase the aluminate phase at the expense of the ferrite phase, thereby compromising the clinker quality. This also imparts harder burning which translates to high fuel consumption [22]. This, therefore, necessitates the beneficiation of Matisaa gray rock for clinker production.

The sulfatisation modulus of Matisaa gray rock ranges from 1.69 – 3.87. This *SM* value of rock is beyond the acceptable limits of $0.8 \leq SM \leq 1.2$ and is attributed to the high SO_3 content in Matisaa gray rock. It implies that the proportion of belite phase in clinker made from Matisaa gray rock will be lower than the proportion of alite phase, and thus low-quality clinker. Thus, beneficiation is required to harmonize the sulphur and alkalis content in Matisaa gray rock. Overall, the raw moduli values of Matisaa gray rock indicate that Matisaa gray rock can be used for clinker production provided it is beneficiated to reduce MgO and SO_3, and enrich Fe_2O_3 and Al_2O_3 to the required level.

4. CONCLUSIONS

In this work, the particle size and raw meal moduli for the standard clinker manufacturing material, Konza kunkur has been compared with a possible clinker material (MGR). It was observed that 69.65% of the particle size composition of Matisaa gray rock was less than 90 μm. Out of this composition, 71.60% of the particle sizes were less than 45 μm. This was comparable to Konza kunkur whose corresponding size composition was 60.0% and 69.65%. These particle size distributions are within the acceptable range and are attributable to the overall specific surface area of 292.5 m^2kg^{-1} and 298.3 m^2kg^{-1} for MGR and Konza kunkur respectively. These SSA values fall within the 250 – 450 m^2kg^{-1} range which is acceptable for cement and thus clinker raw materials. From the study of raw meal moduli characteristics, it shows that Matisaa gray rock, without beneficiation, would lead to the production of low-quality clinker. Except for CaO and SiO_2, the other oxide proportions necessitate beneficiation for the production of high-quality clinker. However, the general parametric comparison of Matisaa gray rock with Konza shows that Matisaa gray rock has the potential for utilization as a clinker raw material.

DISCLAIMER

The products used for this research are commonly and predominantly found in our study area and country. There is no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by the personal efforts of the authors.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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