
Mineral Processing: Production of Calcium Oxide from Nkalagu Limestone, Effect of Particle Size and Temperature

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Abstract

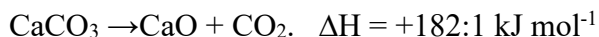
Nkalagu limestone is a commercial raw material for cement production in south eastern Nigeria. The limestone was evaluated for quicklime production using oxidation kiln. The response of particles size was evaluated using five (5) particle size variations of 180 μ m, 355 μ m, 710 μ m, 850 μ m and 1,400 μ m. at temperatures(T) such that $800 \geq T \leq 1200$ and $\Delta T = 100^\circ\text{C}$. The composition of the limestone was evaluated using the Atomic Absorption Spectroscopy (AAS), Simple Electron Microscope (SEM) and Fourier Transform Infra-Red spectroscopy (FTIR). Results obtained confirmed the importance of surface area as conversion was higher same as loss on ignition with smaller particle sizes. SEM analysis reveals the product above 950 $^\circ\text{C}$ as cement clinker and not CaO. Higher temperatures cause the thermal interaction of associated metallic oxide impurities which normally act as fluxes, decomposing the CaO to cement clinker. Above 900 $^\circ\text{C}$, product obtained had a higher bulk density, lower apparent porosity, cake-like and dark. To obtain CaO from Nkalagu Limestone, temperature in excess of 950 $^\circ\text{C}$ is not advised.

Keywords: *Nkalagu limestone, CaO, Temperature, Particle size, calcinations.*

Introduction

Calcium Oxide is produced commercially in a rotary kiln where limestone particles (0.1 – 0.5mm) are sintered at defined conditions of temperature and resident time. Exposing quicklime to high temperature in the kiln for a long residence time results in surface area $< 2 \text{ m}^2/\text{g}$ due to sintering of reactive sites [Oates, 1998]. Today, lime is used in agriculture (soil conditioning), food processing, disinfecting and disease control, water treatment, flue-gas desulfuration, producing steel, plastic and glass, and sugar refining (Boynton 1980). Lime in combination with pozzolanic material can be used as an alternative cementitious material to portland cement. This type of cement can be used successfully for most purposes other than structural concrete work, i.e. in plaster, mortar, production of building blocks, screeds etc. Some types of pozzolanic materials are: pulverized fuel ash, blast furnace slag, volcanic ash, diatomaceous earth, under-fired clay bricks, porcellanite and others. Each has a particular form in which it is most effective as a pozzolana.

Lime and limestone are used in agriculture to neutralize the acidity of the soil and to promote effective use of added fertilizers. Other uses are: water purification, sugar refining, tanning, neutralizing acid mine water, oil well drilling, wire drawing, paper and pulp production, sewage treatment, metallurgical processing, petroleum refining, calcium silicate brick production, paint production and others. Numerous factors influence such properties of CaO: e.g., particle size, porosity, defect density, and purity of calcium carbonate (limestone) (Fox and Soria-Ruiz 1970; Boynton 1980; Fuller and Yoos 1987), burning temperature (Maciejewski and Oswald 1985), retention time (Boynton 1980), and Pressure of CO₂ (Beruto et al. 1984; Wilburn and Sharp 1993). Calcination time increases with increase in particle size (Boateng, 2005; Kumar et al, 2007). The calcination reaction is endothermic



Which suggest higher temperatures favouring the forward reaction. In commercial practice, the calcination process uses a direct-fired rotary kiln powered by coal or natural gas. The particle size of the feed limestone is ≤ 10 cm and has a specific surface area of $\leq 1 \text{ m}^2/\text{g}$. The calcination temperature is generally above 900°C and the duration of calcination ranges between 2 to 4 hours. Quicklime produced commercially under such conditions has a low surface area ($< 2 \text{ m}^2/\text{g}$) [Oates, 1998]. The time-temperature history during calcination reactions greatly impacts the conversion of the raw limestone to quicklime and the surface area of the formed quicklime. Partial pressure of CO_2 in the calcination gas determines the decomposition temperature of limestone and the rate at which the calcination reaction proceeds. The high calcination temperature and the long residence time in the kiln are the main reasons for the low surface area of the lime products. These factors contribute to grain growth by sintering, whereby the individual lime grains in a particle adhere to each other resulting in grain growth and a lower surface area per mass of particle [Oates, 1998].

Raw Materials come in sizes that require alteration to get needed size range. Consequently, there a need to either decrease or increase the particle size. Coarse materials possibly in the form of large rocks are pulverized using ball mills, Jaw crushers or others means possible to obtain powders of desired fineness. The choice of machine and method depends, not only on the size of the feed and of the product, but also on such properties as crushing strength, density, brittleness and plasticity. The major challenge of material grinding, such as limestone, is high silica, feldspar, calcite and other associated impurities. Many of these materials are siliceous, which are glassy and difficult to pulverize due to hardness. This causes high burn ability, high temperatures, incomplete conversion, poor product quality, increase in production cost and increase in emission of flue gas with greenhouse effect. The increasing demand of CaO in Nigeria is met through importation despite the vast deposits of limestone, the primary raw material for its production.

Limestone deposits are found in Some states which includes Nkalagu (Ebonyi), Ewekoro, Shagamu (Ogun State),Ukpilla (Edo State), Ashaka (Bauchi), Sokoko (Sokoto State), mfamosin(Cross River) and Gombe State. Production of quicklime from this nkalagu limestone has not been reported. This work seeks to study the effectiveness of this nkalagu limestone in quicklime production using the commonly available oxidation kiln and comparing same with commercially available quicklime.

Materials and Methods

50kg Lumps of Nkalagu limestone was obtained from the location and brought to the Ceramics engineering research laboratory of Projects Development institute (PRODA), for analyses and production of quicklime. Interest was mostly on the thermal behavior of this limestone to obtain quicklime.

Methods

Particle size characterization

The jaw crusher was used to break the lumps into smaller coarse particles for easy handling and particles segregation. An Electrical Magnetic sieve shaker with sieve sizes of interest was now used to separate the samples into various particle sizes base on sizes passing the immediate but being retained by the next.

Sample preparation for chemical analysis

The raw lump was pulverized and a representative sample was analyzed using AAS. A known mass of the dried sample was measured and digested with Aqua-Regia (Hydrochloric acid: Nitric acid in a ratio 3:1). After the hot digestion using a heating mantle, a known volume of Hydrofluoric acid was added to ensure complete digestion. The digested mixture now clear was then filtered using whatmann No 5 filter paper and water was added to the filtrates obtained and made to standard volume for AAS analysis. The residue obtained was ashed at 500°C to constant weight in a platinum crucible and the non-combustible component obtained was used for silica determination.

Heating Process

The heating process consisted of three steps:

- A total of 25 samples were heated, 5 samples at every temperature corresponding to the particles sizes of 180 μ m, 355 μ m, 710 μ m, 850 μ m and 140mm. The experimental temperatures were 800 $^{\circ}$ C, 900 $^{\circ}$ C, 100 $^{\circ}$ C, 1100 $^{\circ}$ C and 1200 $^{\circ}$ C respectively at +5 $^{\circ}$ C/min.
- After calcining to target temperature, soaking time of 30 min was set to maintain the samples at the constant temperature in order for the whole sample to achieve uniformity in temperature distribution in the furnace.
- At the exhaustion of the soaking time, furnace was shut down and allowed to cool to room temperature before samples were removed for further analyses.

Quicklime yield calculation

$$Yield (\%) = \left(\frac{W_f}{W_I} \right) \times 100 \quad (1)$$

$$Loss\ on\ Ignition (\%) = \left(\frac{W_i - W_F}{W_I} \right) \times 100 \quad (2)$$

Results and Discussion

Oxides Composition analysis.

Tables 1 and 2 shows the uncalcined and calcine sample (Quicklime) were predominantly CaO, SiO₂ and Al₂O₃.

Table 1.0: Chemical profile of Nkalagu Limestone before calcination.

Elements	Composition (%)	ASTM specification for Cement Production(Akinniyi and Ola, 2016)
SiO ₂	5.64	4
Al ₂ O ₃	0.418	0.77
Fe ₂ O ₃	0.182	0.33
K ₂ O	0.323	0.02
CaO	50.27	51.40
MgO	0.812	1.3
Na ₂ O	0.005	0.01

Table 2.0: Chemical profile of the quicklime produced from calcinations of Nkalagu limestone

Oxide	Average Weight (%)
SiO ₂	24.92
Al ₂ O ₃	8.38
Fe ₂ O ₃	0.27
K ₂ O	0.41
CaO	62.12
MgO	1.34
Na ₂ O	0.06
SO ₃	1.51

Results obtained are comparable with report of Udeh etal, 2021. .The value obtained for Fe₂O₃ was very low, much below 1.7% which accounted for why the calcined sample was light ash in colour.

Loss On Ignition (L.O.I)

The smaller particle materials had a higher percentage of weight change and by implication, higher conversion rate as shown in Figure 1. Reduction in particle size or comminution is necessary to increase the surface area because, in most reactions involving solid particles, the rate of reactions is directly proportional to the area of contact with a second phase.

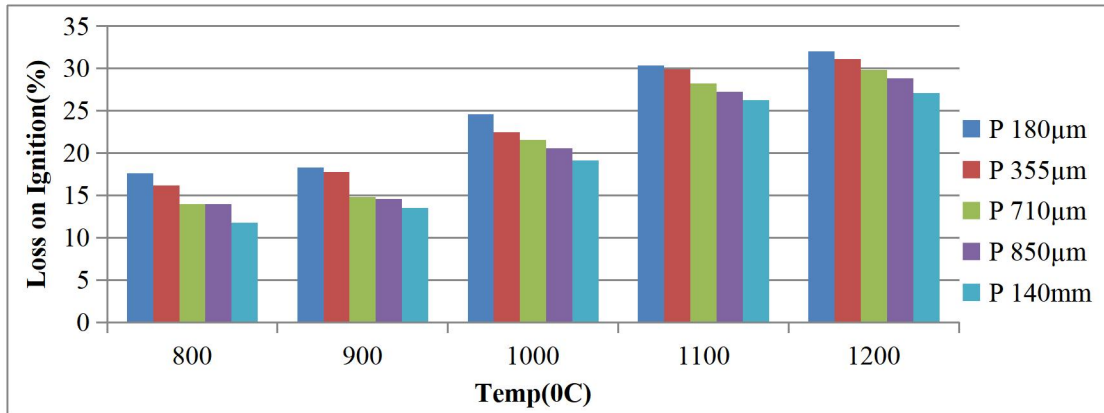


Figure 1 Response of L.O.I to variation in Temperature.

The higher the temperature the higher the percentage loss in ignition and also the smaller the particle size the higher the percentage loss on ignition. This is expected since high temperature translates to high burn ability of limestone. This high burn ability is synonymous with high disintegration of limestone into CaO and CO₂. The high release of CO₂ to the environment also implies high loss on ignition with increasing temperatures and decreasing particles sizes.

Effect of Temperature on Conversion of CaCO₃ to CaO

Figure 2.0 shows a pronounced loss from 900 -1100°C. This could be due to thermal disintegration of the CaO, volatilization of associated Mineral elements and flue gases present in the raw material (limestone). The nature of the product obtained from this Nkalagu limestone at these temperatures showed a great variation in physical appearance from the CaO obtained at ≤900°C. As temperature increases from 800°C to 900°C, debonding process of mineral particles also increases as many fragments are stripped from the matrix (Yan-jun et al, 2018). Consequently, there is reduction in grain size, increase in the number and length of cracks with increase in temperature. During heating from ambient temperature to about 400°C, there is mass loss due to loss of organics, dehydration reaction and pore water evaporation. The absorbed water, bound water, and little mineral water existing in the voids or original defects would generally escape during this period (yan-Jun et al,2018; Dong et al,2014).

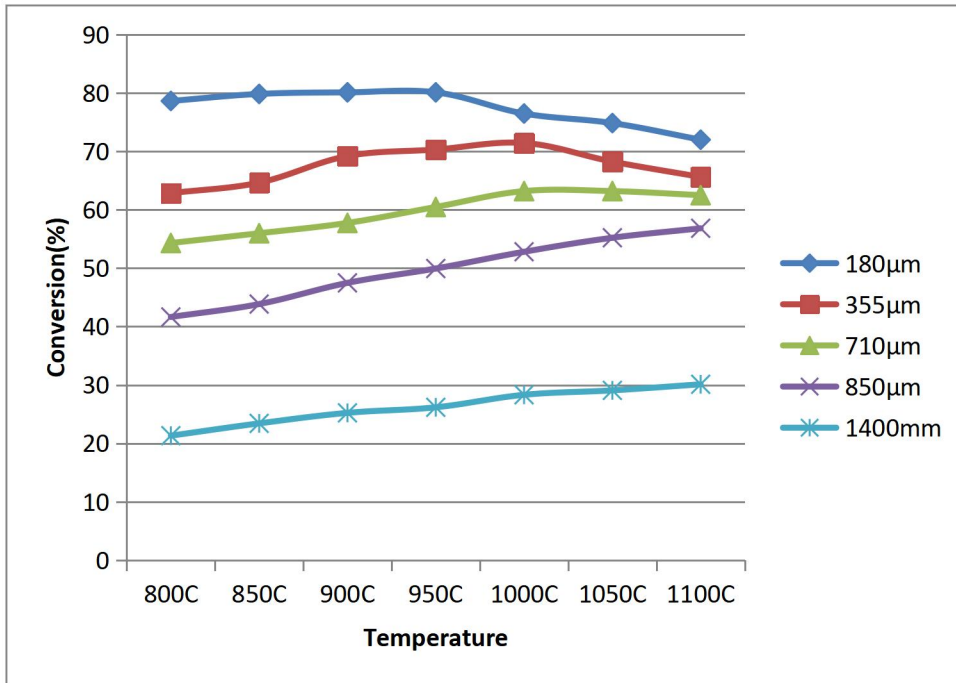


Figure 2.0: Profile of response of particle sizes to temperature

From figure 2, we observe that 180µm Particle Size distribution had the highest conversion rate, decomposition rate and hence the need to maintain particle size distribution at $\leq 180\mu\text{m}$ to achieve the desired promptness in lime conversion. This observation corroborates previous reports that the burn ability of any material mainly depends on the chemical composition of the material, Mineralogical characteristics and Particle size (Suleiman et al, 2013). It is needful to achieve the right particle size for easy burning of limestone, reduction in global warming due to emission from burning, reduction in fuel consumption, reduction in excessive heat radiation, good quality lime and decrease in production cost.

Effect of Particles size

Figures 3-7 reveals that for every particle size studied at experimental temperatures, the finer the particle size, the higher the percentage conversion but from 1000°C to 1100°C, the CaO yield was significantly reduced indicating a Loss of reactivity of lime caused by over burning due to high temperature and high soaking time. When limestone is heated, CO₂ is release which creates pores in the limestone matrix, creating extra surface area for series of chain reactions to occur. Excessive burning beyond the required temperature range results in the collapse of these pores, thereby reducing hydration potential of lime with water (Suleiman et al, 2013).

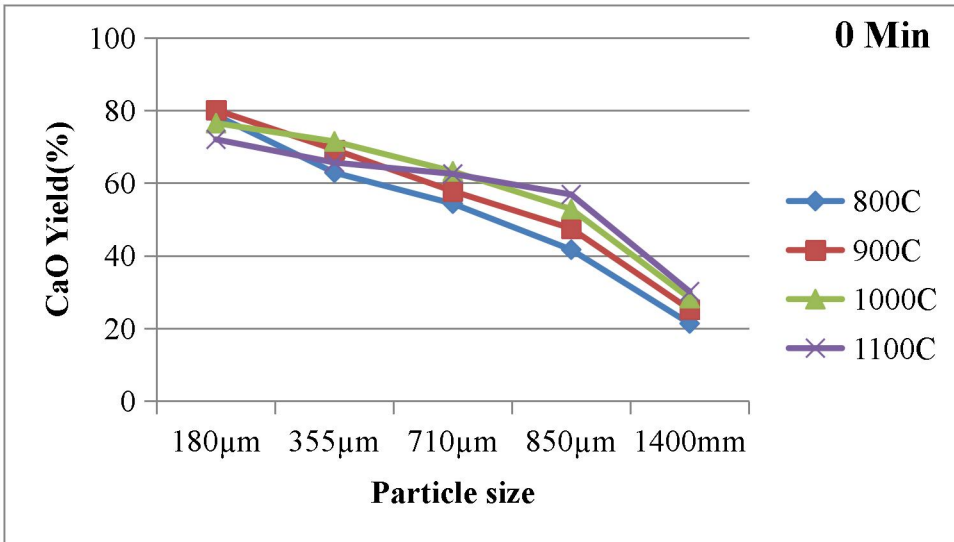


Figure 3 Response of CaO yield to Particle size at O-Min

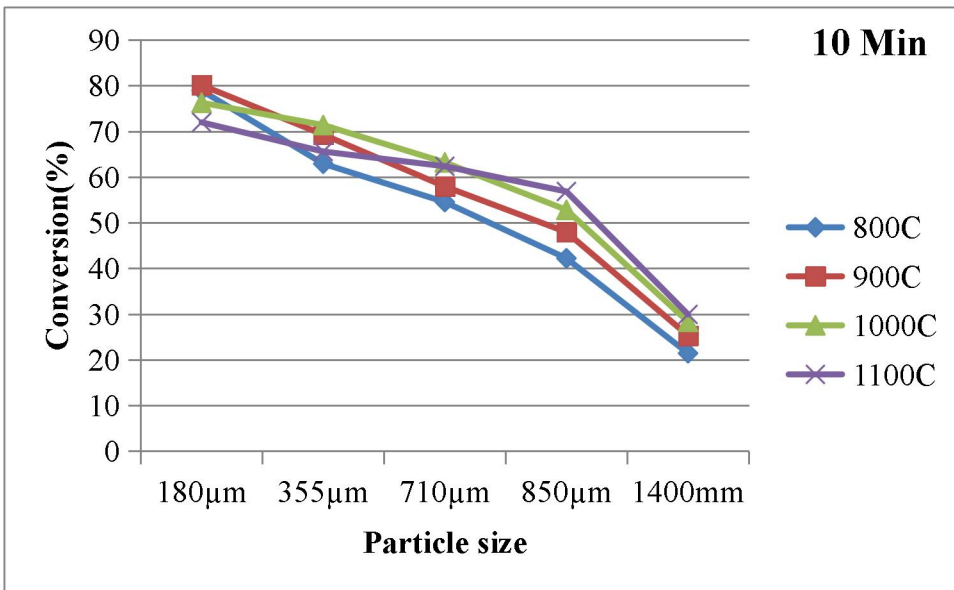


Figure 4 Response of CaO yield to Particle size at 10 min

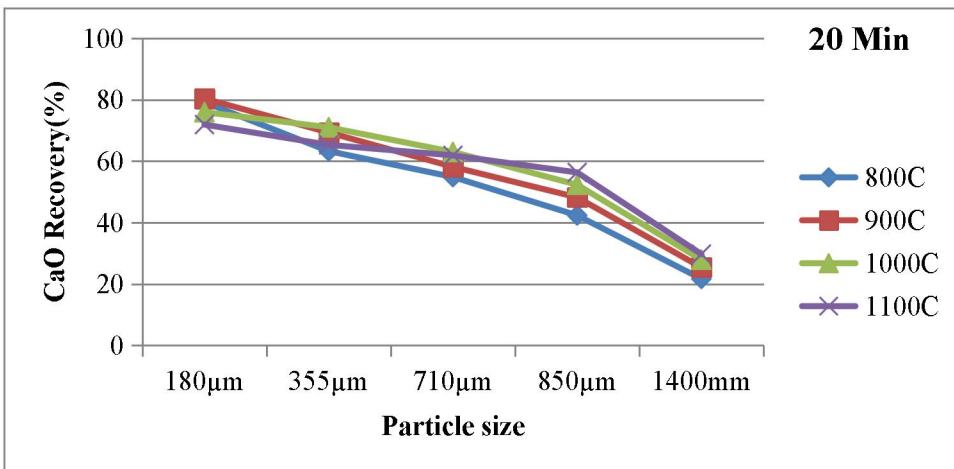


Figure 5 Response of CaO yield to Particle size at 20 min

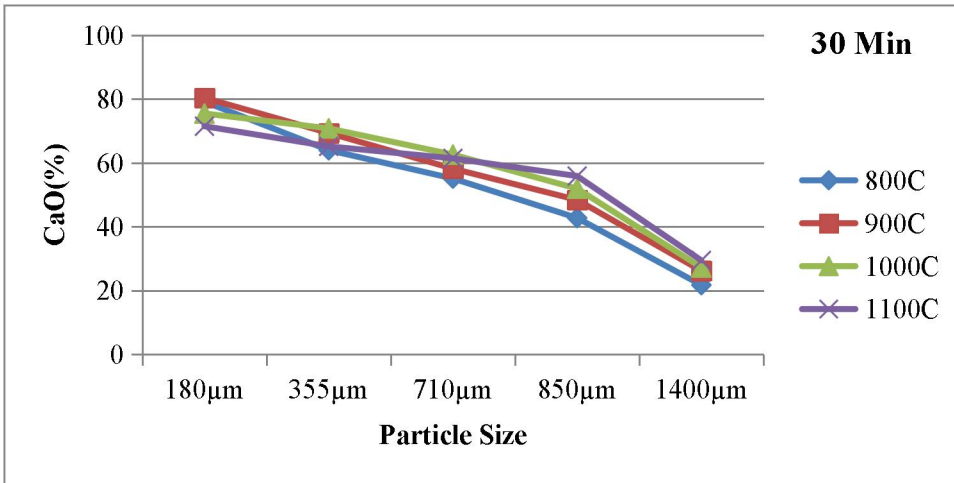


Figure 6 Response of CaO yield to Particle size at 30 mins

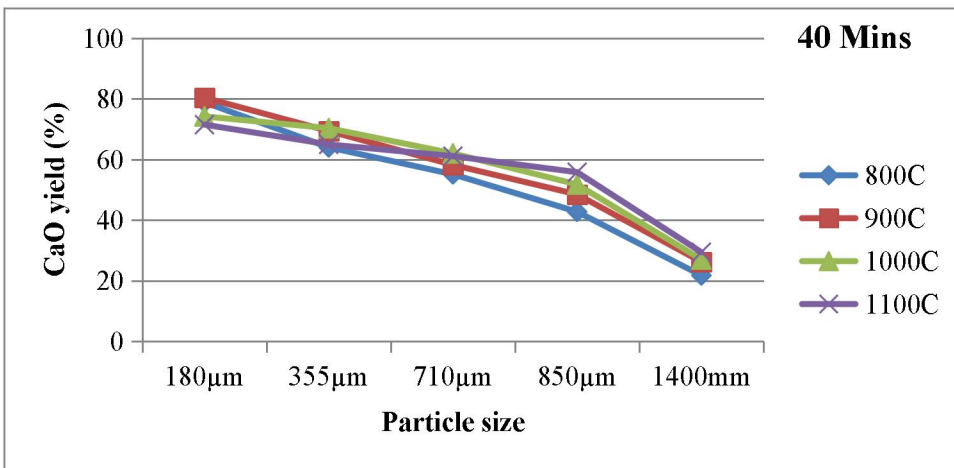


Figure 7 Effect of particle sizes on CaO recovery.at 40 mins

Products obtained at 1000⁰C to 1100⁰C were different in physical appeal and stickiness as their colours changed to dark ash and at room temperature for two weeks became hygroscopic and hardened to form of lumps. This is because over burning at such temperatures results in melting of associated impurities in the lime (mainly silica, alumina and iron, MgO, K₂O et.c). Most of these associated impurities act as low temperature fluxes increasing the bulk density and reducing the porosity of the material forming cement clinker, further reducing the calcium content available for reaction with water. This observation was independent of particle size used in this study.

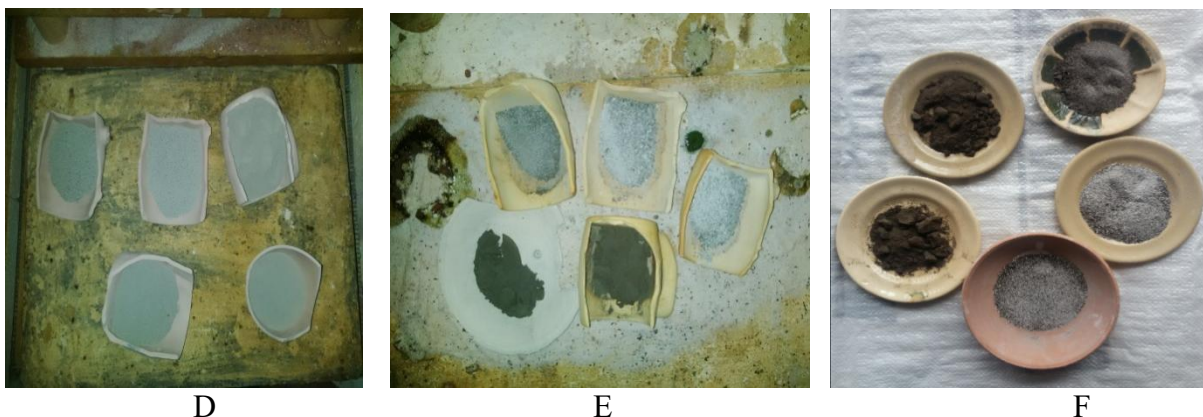


Plate 1 D – Samples inside the Kiln before Calcination. E – Samples after Calcination. F – Samples on display. The heated samples upon removal from furnace were physically inspected for changes in colour, texture, weight, hygroscopicity (stickiness)

Effect of Soaking Time:

All the samples of different particle sizes heated at 800 – 900°C showed slight increase in CaO yield in increase in soaking time as shown in Figures 8 – 9. From Figures 10 – 11, larger particle sizes(850µm and 1400µm) showed slight increases at higher temperature and soaking time which could be due to lower surface area of contact between aggregates and temperature which increased with increase in soaking time.

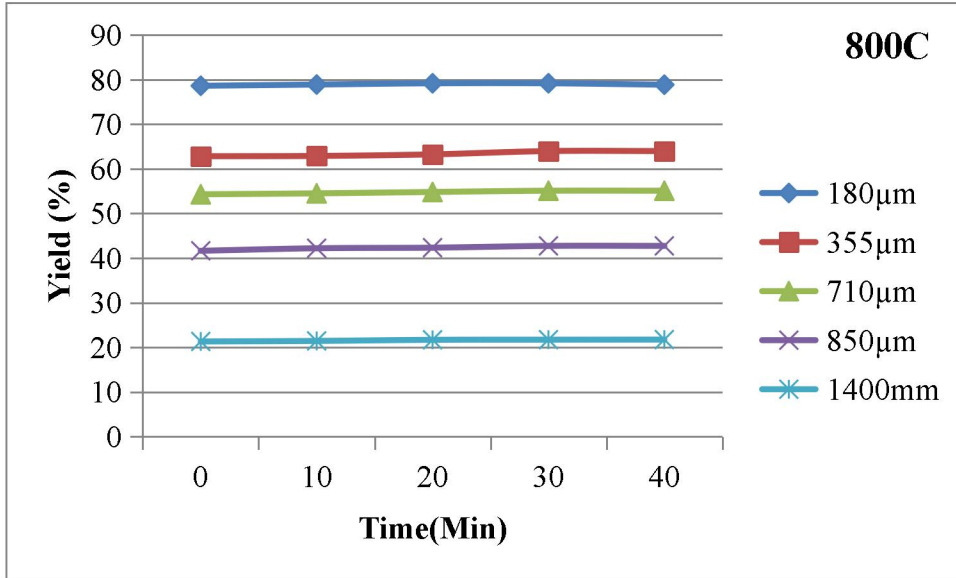


Figure 8 Response of CaO yield(%) to soaking at 800°C

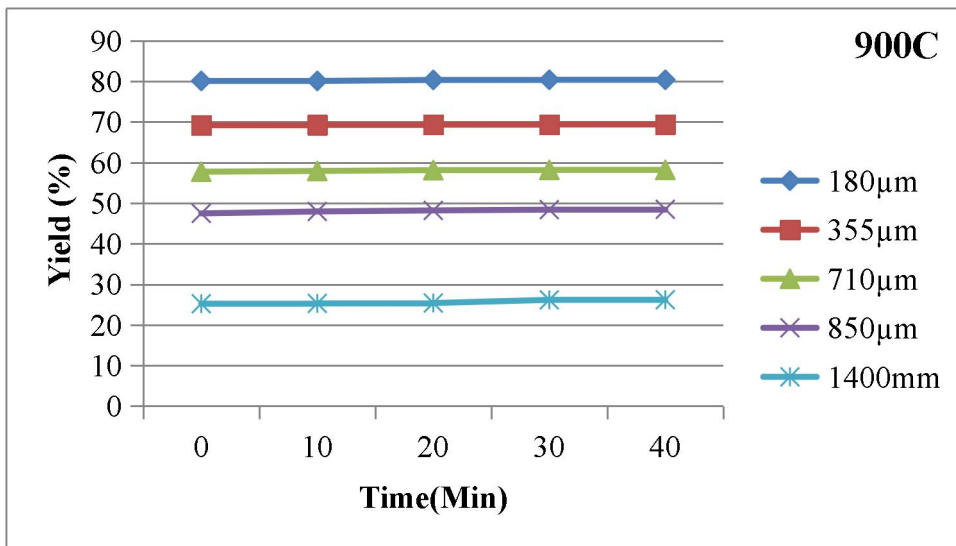


Figure 9 Response of CaO yield(%) to soaking at 1000°C

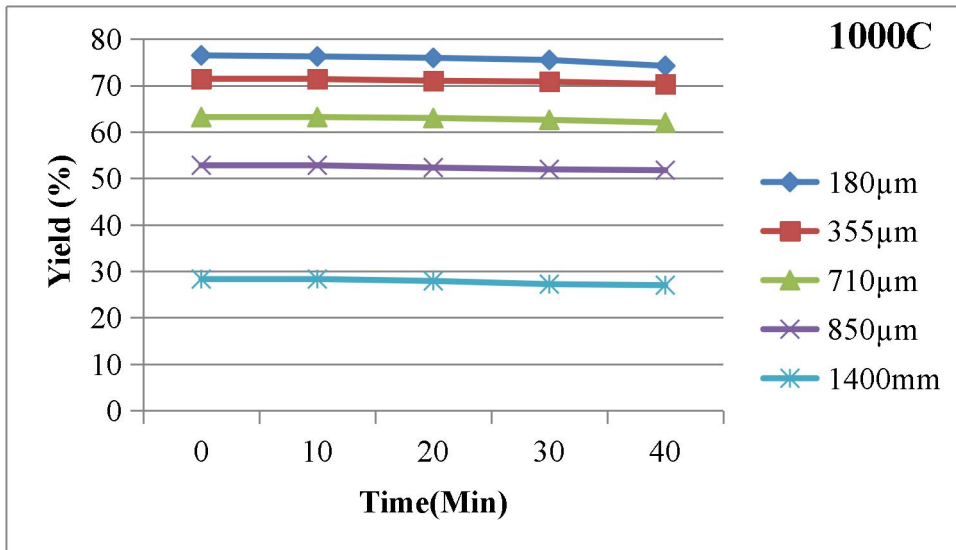


Figure 10 Response of CaO yield(%) to soaking at 1000°C

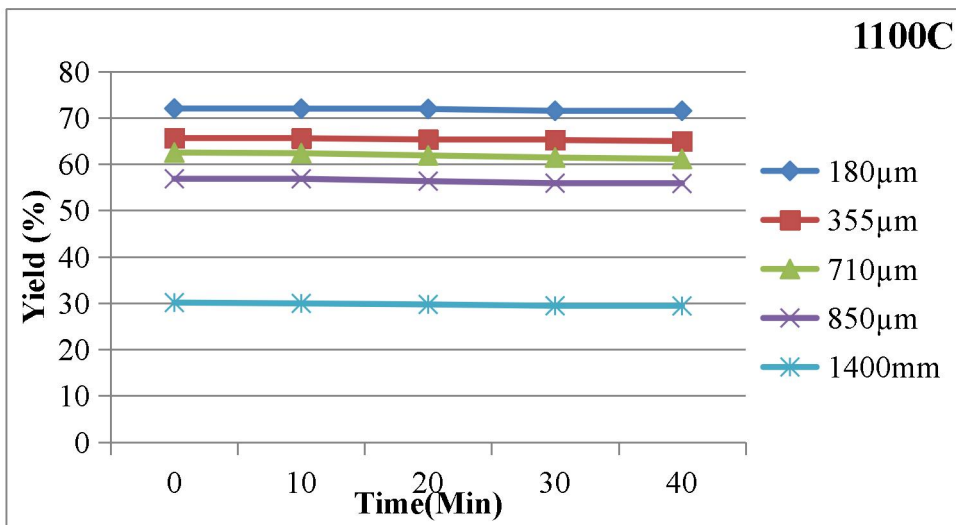


Figure 11 Response of CaO yield(%) to soaking at 1100°C

The finer samples(180, 355 and 710µm) showed decrease in yield(%) at soaking time above 20mins as shown in figures 10 and 11 respectively. As explained earlier, this is due to loss of reactivity caused by over-burning, resulting in melting of associated impurities in the lime such as SiO₂, Al₂O₃, Fe₂O₃/FeO, MgO, K₂O et.c). These associated impurities are low temperature fluxes which aid the formation of cement clinker, further reducing the calcium content available for reaction with water.

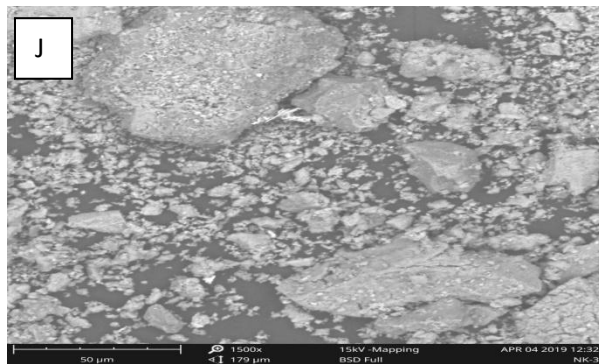
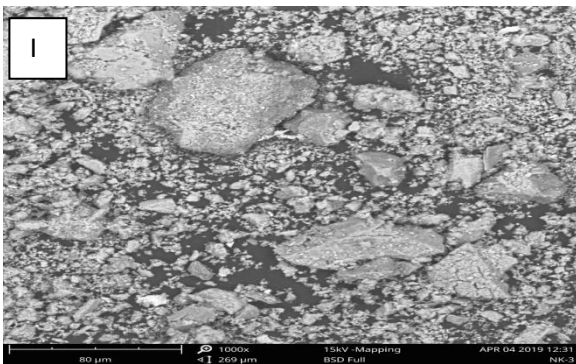
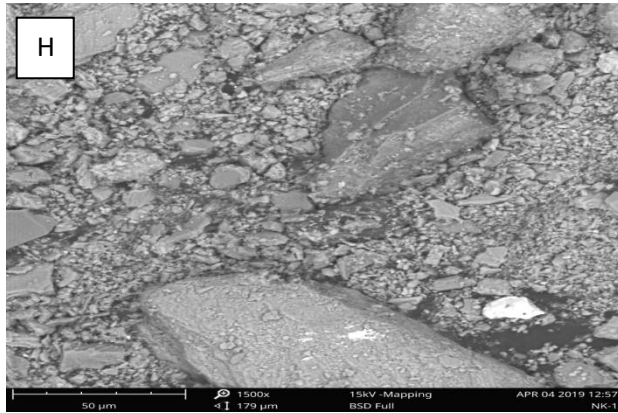
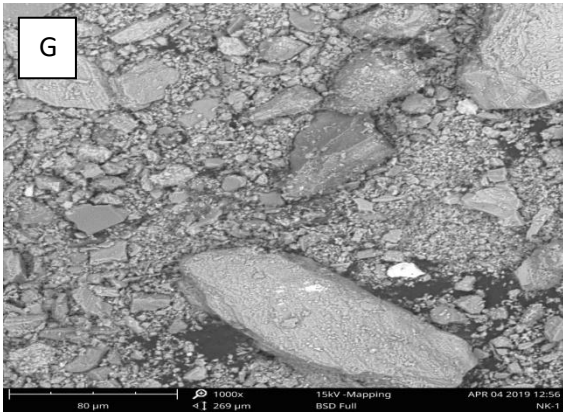
Fourier Transformed Infra-Red spectroscopy(FTIR) analysis of raw sample and products

Raw Limestone peaks	Peaks @ 900°C	Peaks @ 1200°C	Inference
	3641.6	3693.8, 3637.9, 3529.8	stretching vibrations of the surface hydroxyl groups (Si-Si-OH or Al-Al-OH) (Rajeb et al, 2017), OH stretching of inner-surface hydroxyl groups consistent with Kaolinite(Russell, 1987).
2877.5, 25122,	2877.5,		C-H stretching vibrations of organics(Ituma et al,

	2322,		2018), O-H stretching mode vibration of Calcite.
2109.7,	2113.4, 2322	2102.2	C \equiv C of alkynes(Abuh et al, 2019)
1997, 1796	1982.9, 1796.6	1982.9, 1792.8	C=O stretching, combinational mode, O-H stretching of Calcite.
1420	1420.1	1408.9	Doubly degenerate asymmetric stretching mode vibration, (CO ₃) ²⁻ stretching mode vibration.
1006.4, 779	916.9, 776.3	1110.7, 991.5	Si-O bonds stretching
875	875.9	872.2	C=O stretching mode vibration
711.9	711.9	711.2	Ca – O bond

The Si-O bonds are the strongest bonds in the silicate structure and can be readily recognized in the infrared spectra of such minerals by very strong bands in the region 900 to 1100 cm⁻¹ is due to stretching as well as less intense bands in the 400 to 800 cm⁻¹ region is due to bending. Quartz is therefore present in all the samples as shown in the table. The symmetric stretching vibrations, observed at 1400-1450 cm⁻¹ are particularly sensitive to the side symmetry for the carbonate group. Bands consistent with Ca – O were observed in all the samples. This suggests that the sample is predominantly CaCO₃ with quartz and Kaolinite as minor components.

Simple Electron Microscope(SEM) Studies of sample and products



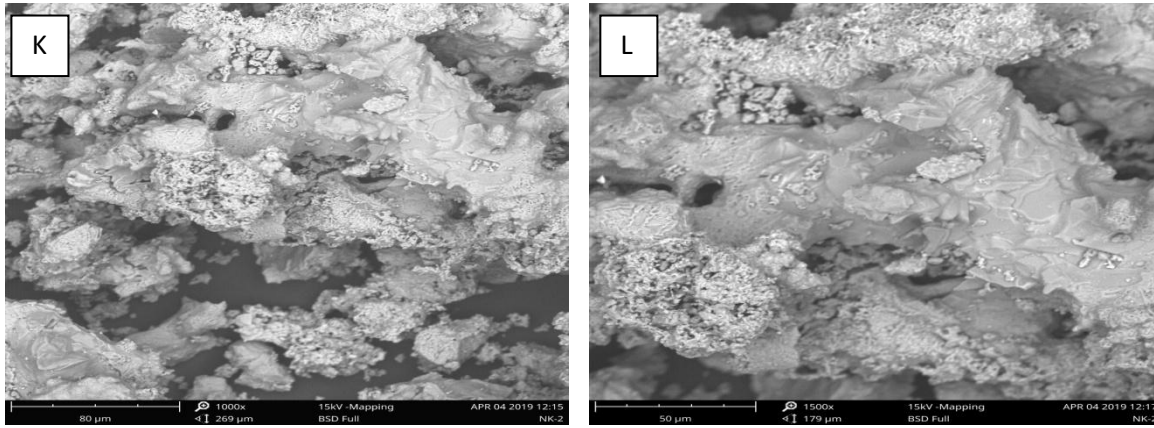


Figure 12: SEM of: (1) Raw Nkalagu Limestone at 80µm(G) and at 50µm(H), (2) Nkalagu limestone calcined to 900°C at 80µm(I) and 50µm(J) (3) Nkalagu limestone calcined at 1000°C at 80µm(K) and 50µm(L).

The microstructures of pulverised materials were observed before and after sintering, and the effect of heat treatment modification was studied. Microstructural differences were observed for the same composition material under the different heating conditions (Figure 12). The raw sample [figure 12 G and H] shows morphology with angular grains of quartz size, covered with fine particles and the grains of calcite can be clearly seen. Figure 12 (I) and (J) show microstructure of CaO obtained by thermal modification of raw limestone. Figure 12 [K] and [L] shows clearly existence of microstructure consistent with clinker. The outer part contains larger alite crystal size and the belite crystals are distributed without any clusters comparing with the inner part. The presence of rounded belite and Euhedral alite in rim layer can be seen. The images are however influenced by the degree of the grinding of the raw material(Kaddourah and Azizi, 1996), burning time, reducing conditions, heating and cooling rate(Ahmadi, 2017)

Conclusion

It is advisable to calcined Nkalagu limestone at temperature, $T \leq 950^{\circ}\text{C}$ when CaO is the material of interest as beyond this temperature, lime breaks down and cement clinker is formed. Particle size is also important in determining the quality of CaO as the smaller the particle size, the higher the conversion and consequently, the higher and purer the quality of CaO. Though rotary kilns are used since they guarantee even temperature distribution, when smaller quantities of CaO are required, muffle furnace and kiln can be used at controlled conditions. The FTIR peaks obtained for raw and calcined products are consistent with CaCO_3 , CaO and quartz with Kaolinite as minor components. Microstructural studies confirm the production of cement clinker at temperatures $T > 950^{\circ}\text{C}$.

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