Article

Analysis of Limestone Samples from Deposits at Selected Nigeria Areas as a Potential Raw Material for the Production of Portland Cement

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Abstract: Analysis of limestone samples from 4 selected areas in Nigeria as a potential raw material for production of Portland cement has been carried out. By means of Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) the decomposition of calcium carbonate were revealed at $853.36^{o}C$; $827,01^{o}C$; $796.12^{o}C$ and $545.10^{o}C$ respectively. The X-ray florescence revealed that the Kalambaina limestone has SiO_2 15.31%; Al_2O_3 4.29%; Fe_2O_3 2.16%; CaO 42.85%; MgO 1.58%; $CaCO_3$ 76.50% and LOI 33.42%; Kware limestone has SiO_2 24.86%; Al_2O_3 7.48%; Fe_2O_3 4.34%; CaO 31.41%; MgO 2.06%; $CaCO_3$ 56.09% and LOI 28.43%; Amanawa limestone has SiO_2 41.50%; Al_2O_3 15.78%; Fe_2O_3 7.43%; CaO 15.28%; MgO 1.78%; $CaCO_3$ 27.30% and LOI 17.34% and Maiyama limestone has SiO_2 48.40%; Al_2O_3 20.52%; Fe_2O_3 9.53%; CaO 6.72%; MgO 1.38%; $CaCO_3$ 12.01% and LOI 12.33%. The mineral composition Ca, Mg, Fe, Cu, Cr, Pb, Na and K were determined for the samples and it was observed that their amount were within the minimum levels for use in the industrial production of Portland cement.

Keywords: Limestone, Portland cement, XRF, TGA/DTA

1. Introduction

Limestone is a common sedimentary rock widely distributed throughout the world in deposits of varying sizes and degrees of purity. Its major compound is calcium carbonate, which is white in colour,

however, the colour of most limestone are in varying shades of grey and tan due to the presence of impurities (Kamile *et al.,* 2009). The common impurities are clay, magnesium carbonate, silica, alumina, iron oxides, sulphates, phosphate and oxide of sodium and potassium, out of these, the main impurities are silicon (from sand)   and alumina (from clay) with iron as the third (Khan and Akhyar, 2004).

There are many deposits of limestone in various places in Nigeria including, Kogi, Edo, Benue, Sokoto, Adamawa, Enugu, Ondo, Ogun, Plateau State and the Federal Capital Territory Abuja (Tsivilis *et al.,* 2000).

Cement is a material with adhesive and cohesive properties which make it capable of bonding minerals fragment into a compact whole, (Toypine *et al.,* 2015)

The cement of used in the making of concrete has the property of setting and hardening under water by virtue of a chemical reaction with it.

The name Portland Cement given due to the resemblance of the colour and quality of the hardened cement to Portland stone Island in England. (Hooton and Michael, 2002). Every year a large amount of Portland cement is produced and used for the 'construction of building, roads and other local purpose (Toypine *et al.,* 2015).

Portland cement is a substance which binds together the particles of aggregates to form a mass of high compressive strength concrete. It is a combination of limestone or chalk with clay mixed in a proportion depending on the type of cement desired (Ige and Adekunle, 2013). The quality and durability of any block or concrete structures depends solely on the quality of the cement to which it was built and in order to achieve the best quality of any cement, analysis of limestone as a raw material for Portland cement would be conducted to determine the chemical compositions of the limestone. Therefore, the present study would focus on the comparative analysis of limestone from Maiyama, Kware, Amanawa and Kalambaina as potential raw material for Portland cement production.

2. Materials and Methods

2.1. Chemical Reagents

The chemicals are used as procured without further purification as they are of analytical grade.

2.2. Sample Collection and Treatment

The samples were obtained from Maiyama in Kebbi state, Kware, Amanawa and Kalambaina in Sokoto state and stored in a dry place in a polythene bag prior to analyses.

2.3. Determination of Constituents Using Wet Analysis
2.3.1. Determination of Loss on Ignition (LOI)

Into a crucible 1.0g of each sample and placed in a muffle furnace and heated at 900ºC for 30

mins. The heated sample was allowed to cool at room temperature in a desiccator and weighed (m_2). The loss in weight was recorded as percentage loss on ignition (Toypine*et al.,* 2015).

$$\% \text{ LOI} = \frac{m_1 - m_2}{m_1} \; x \; 100 \quad \text{………………………………………..………………} \quad (1)$$

2.3.2. Determination of silica (SiO₂)

Exactly 1.0g of sample and 5.0g of sodium carbonate was mixed thoroughly in a crucible and ignited in furnace at 950°C for 30 min. The crucible was cool down to ambient temperature in a desiccator. The crucible was placed in a 500cm^3 beaker and 20cm^3 of HCl was added to remove the mixture in the crucible and the crucible was washed 4-5 times with distilled water. The beaker was transferred to the sand bath for drying and after drying; 1.0 g of NH$_4$Cl and 20cm^3 of HCl was added and allowed to digest for some minutes. The solution was filtered into a Whatman No. 40 filter paper and stored under ambient temperature in a water bath. The filter paper was transferred to an empty crucible of known weight (W$_1$) and ignited in a furnace at the temperature of 1000°C for 30min. It was cooled down to ambient temperature in a desiccator and weigh again (W$_2$). The difference in weight was recorded as % SiO$_2$ (Khan and Akhyar (2004).

$$\% \text{SiO}_2 = (\text{Final weight } (W_2) - \text{Initial weight } (W_1)) \text{ x } 100 \text{……………………. .(2)}$$

2.3.3. Determination of calcium carbonate (CaCO₃)

About 1g of sample was weighed into 250cm^3 conical flask and 25cm^3 of 1M HCl (standardized) was added and heated on a hot plate until boiling. The solution was rinsed with distilled water and 2-3 drops of phenolphthalein was added and titrated until endpoint (change in colour to pink) with standardized 0.5M NaOH. The % CaCO$_3$ was calculated using the formula below (NlS, 2003):

$$\% \text{CaCO}_3 = (25 - \text{x/2}) \text{ x } 5.005 \text{…………………………………………..} \quad (3)$$

2.3.4. Determination of lime (CaO)

Precisely 50cm^3 of filtrate from the SiO$_2$ determination was pipetted into 300cm^3 beaker and diluted up to 200cm^3 mark with distilled water and the beaker was placed in a hot plate and stirred. The solution was adjusted to pH 5 by adding 25% KOH drop by drop then 10cm^3 of triethanolamine and 20cm^3 of 25% KOH was added into the solution followed 2g of calcon indicator. The solution was titrated with EDTA solution until end (from red violet to clear blue) and %CaO was calculated using to the equation below (HCG, 2003):

$$\% \text{CaO} = \text{V x } f_{\text{CaO}} \text{……………………………………….. ….} \quad (4)$$

Where V is the volume of EDTA used to reached end point

F_{CaO} is the factor given in the container of strong EDTA

2.3.5. Determination of MgO

Exactly $50 cm^3$ of filtrate from the SiO_2 determination was pipetted into $300 cm^3$ beaker and diluted up to $200 cm^3$ mark with distilled water and the beaker was placed in a hot plate and stirred. The solution was adjusted to pH 5 by adding NH_3 drop by drop then $10 cm^3$ of triethanolamine and $10 cm^3$ of NH_3 was added into the solution using dispensette followed by 2g of mixed indicator (the colour changes to violet). The solution was titrated with EDTA solution until end (from violet to colourless) and %MgO was calculated using to the equation below (HCG, 2003):

$\%MgO = V \times f_{MgO}$……………………………………………… (5)

Where V is the volume of EDTA used to reached end point

F_{MgO} is the factor given in the container of strong EDTA

2.3.6. Determination of Fe₂O₃

Exactly $100 cm^3$ of filtrate from the SiO_2 determination was pipetted into $500 cm^3$ flask equipped with magnetic stirrer and 3-5 drops of bromophenol was added followed by 3-5 drops of NH_3 until colour change to pale blue. $20 cm^3$ of 0.1M HCl and $15 cm^3$ of buffer solution was added by means of dispensette to the solution. 3-5 drops of salicyclic acid and the solution was heated to a temperature of 60^oC then titrated with weak EDTA until endpoint is reached (pink to clear yellow). The $\%Fe_2O_3$ was calculated using to the equation below (HCG, 2003):

$\%Fe_2O_3 = V \times f_{Fe2O3}$……………………………………………. (6)

Where V is the volume of EDTA used to reached end point

f_{Fe2O3} is the factor given in the container of weak EDTA

2.3.7. Determination of Al₂O₃

About 3-5 drops of concentrated acetic acid was added to the solution used for analysis of Fe_2O_3 (above) until the color changes to pale blue. 3-5 drops of complexion indicator and 3-5 drops of PAN indicator were added. The solution was heated to boiling point and titrated with EDTA solution until the endpoint is reached (color changes from pink to clear). The $\%Al_2O_3$ was calculated using the equation below (HCG, 2003):

% Al_2O_3 = V x f_{Al2O3}………………………………………….. (7)

Where V is the volume of EDTA used to reached end point

f_{Al2O3} is the factor given in the container of weak EDTA\

2.4. X-Ray Fluorescence (XRF)Analysis of Limestone

Exactly 1.2g of sample and 8.4 g of dilithiumtetraborate was thoroughly mixed in a plantinum crucible and heated in a furnace at 950°C for 30mins. The content of the crucible was molded and cooled to obtain a glass bead. It was then subjected to XRF analysis (Ali *et al.,* 2008).

2.5. Thermo-Gravimetry Analysis (TGA)/Differential Thermal Analysis (DTA)

In the analysis 26.276g of sample was used then dried overnight in a force air oven at 40°C. Thermal analysis of the samples was conducted on a simultaneous DSC-TGA instrument at 5°/min from 25°C to 800°C in 100 mg/min (Roman et al., 2005).

2.6. Determination of Metals Compositions (Ca, Mg, Fe, Pb, Cr and Cu) by AAS

Exactly 2g of sample was ashed in a muffle furnace at 950°C. The resulted ash was dissolved in 5cm^3 of   nitric acid (HNO_3)   and   4 cm^3 of perchloric acid ($HClO_4$) were added and slightly stirred. It was heated on a hot plate and a strong effervescence was produced. When the brown fumes were less dense, the solution was allowed to cool. The solution was filtered and diluted up to 50 cm^3 of distilled water and filtered. The filtrate was used for analysis of metal contain (Ca, Mg, Fe, Pb, Cr and Cu) using Atomic Absorption Spectroscopy Standard Procedure describe by (Roman *et al.,* 2005)

2.7. Analysis of Sodium and Potassium using Flame Emission Spectroscopy (FES)

Flame Emission Spectroscopy has similar properties with AAS, but they differ from each other in terms of measurement of transmitted radiation. Potassium and Sodium solutions when sprayed as a fine mist of droplets (nebulized) into a non-luminous gas flame burner, the sodium and potassium metallic ions are atomized and get excited to higher energy level. On returning to ground state, the excited atoms emit radiation of characteristic wave length (590 nm for sodium and 770 nm for potassium). The light then passes through a suitable filter into photosensitive detector and the amount of current produced was measured, which is proportional to the concentration of the potassium or sodium present in the sample.

The flame photometer was stabilized for 30mins before the galvanometer was adjusted to zero with distilled water and then to full scale with standard solution of 25ppm. The other standard solutions were subsequently aspirated alongside with the blank and sample solutions. Calibration curves were

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plotted from which the concentrations of sodium and potassium in the sample were determined and their actual concentration calculated using the equation below

$$\text{Conc.(mg/100g)} = \frac{X(ppm) \times Vol.of\ sample\ made}{Weight\ of\ sample \times 1000}\ x100 \quad \ldots\ldots\ldots\ldots(8)$$

3. Results and Discussion

3.1. XRF Analysis

The results shown in table 1 below for the composition of the samples determined using XRF analysis indicated that highest values of SiO_2, Al_2O_3, and Fe_2O_3 were observed in the Maiyama sample. Highest values of CaO and L.O.I were found in the Kalambaina sample, while the highest values of MgO and $CaCO_3$ were found in Kware and Kalambaina samples respectively. According to (Nigerian Industrial Standard, 2003), the percentage $CaCO_3$ in limestone used for low grade cement should be 65-75% while for high grade cement should be 76-99%. As shown in Table 1, the percentage $CaCO_3$ using XRF analysis in limestone samples from Amanawa (27.30%), Maiyama (12.01%) and Kware (56.09%) are below the range recommended values by NIS (2003), while Kalambaina (76.50%) is within the range recommended value by NIS (2003).

Table 1: Composition of the samples determined using XRF analysis (%wt)

Parameter	Kalambaina	Kware	Amanawa	Maiyama
SiO_2	15.31±0.06	24.86±0.05	41.50±0.04	48.40±0.02
Al_2O_3	4.29±0.02	7.48±0.02	15.78±0.02	20.52±0.04
Fe_2O_3	2.16±0.02	4.34±0.02	7.43±0.02	9.53±0.02
CaO	42.85±0.04	31.41±0.03	15.28±0.04	6.72±0.02
L.O.I	33.42±0.02	28.43±0.02	17.34±0.04	12.33±0.02
MgO	1.58±0.02	2.06±0.02	1.78±0.02	1.38±0.02
$CaCO_3$	76.50±0.02	56.09±0.02	27.30±0.02	12.01±0.02

Key: L.O.I. = Loss on ignition

3.2. Wet Analysis

The chemical composition such as $CaCO_3$, CaO, MgO, Fe_2O_3, Al_2O_3, SiO_2 and LOI were found in all the limestone samples investigated from Kalambaina, Kware, Amanawa and Maiyama.

Figure 1 presents the percentage composition of $CaCO_3$ using wet analysis in limestone samples of Kware (54.37 %), Amanawa (21.36 %) and Maiyama (4.61 %) are lower in both recommended value by NIS (2003) and the results obtain for Kware (56.09%), Amanawa (27.30%) and Maiyama (12.01%)

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as shown in Table 1. More so, the result in Figure 1 for Kalambaina (64.04 %) is lower than the one presented in Table 1 for kalambaina (76.50 %) but within the recommended value by NIS (2003) for low grade cement. It is however, recommended by NIS (2003) that the difference between XRF analysis and wet analysis should not be more than 12 %. The percentage calcium below the range recommended affects the quality of the cement such as workability and setting time (Bonavetti et al., 2003).
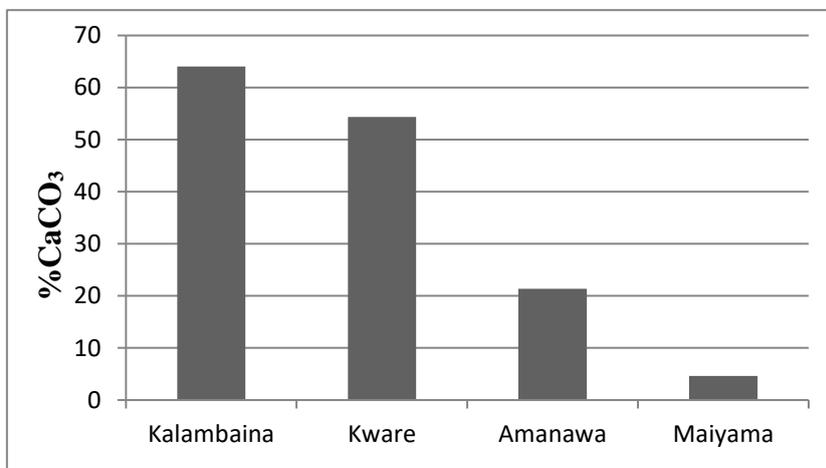
Figure 1: Composition of $CaCO_3$ in different samples determined using wet analysis

According to NIS (2003), percentage CaO in limestone used for cement production should be 38-49%. As presented in Table 1 the percentage CaO using XRF analysis in limestone sample from Kware (31.41%), Amanawa (15.28%) and Maiyama (6.72%) are below the range recommended by NIS (2003).This could affect chemical reactions in the clinker (Benachour et al.,2008). However, CaO content of sample from Kalambaina (42.85%) is within the range recommended by NIS (2003) for cement production. Also, Figure 2 presents the percentage composition of CaO using wet analysis in limestone samples of Kalambaina (52.5 %), Kware (30.5 %), Amanawa (21.2 %) and Maiyama (9.46 %).
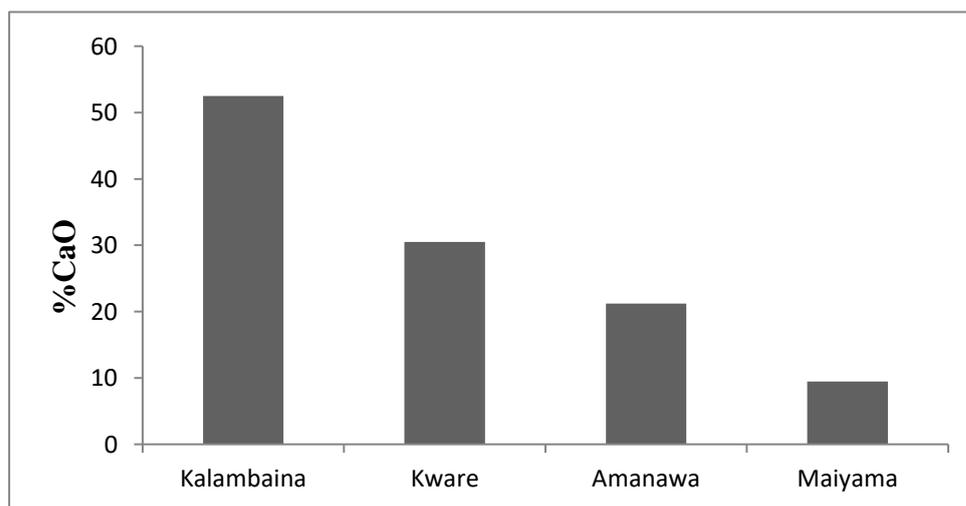
Figure 2: Composition of CaO in different samples determined using wet analysis

These values are lower than the recommended range by NIS (2003). Limestone with less than 2% MgO is used for paper manufacturing (Khan and Akyar, 2004). MgO content of Kalambaina (1.58%), Maiyama (1.38%) and Amanawa (1.42%) are within recommended value by NIS (2003).

According to NIS (2003), the percentage MgO in limestone used for cement production should be 1.0-1.4%. As shown in Table 1 the percentage MgO using XRF analysis in limestone samples from Kalambaina (1.58%) and Kware (2.06%) are above the range recommended by NIS (2003), while Amanawa (1.42 %) and Maiyama (1.38%) are within the range recommended by NIS (2003). Figure 3 also presents the percentage composition of MgO using wet analysis in limestone samples of kalambaina (9.39) and Kware (13.15 %) are higher in both the recommended standard by NIS (2003) and the result obtain in XRF analysis for kalambaina (1.58 %) and kware (2.06 %). Thus, the result obtain for Amanawa (0.38%) and Maiyama (1.3 %) in figure 3 are lower when compared with recommended standard by (NIS, 2003). MgO are secondary oxide i.e. they are not considered as potential composition of clinker compounds. High MgO above 1.0-1.4% affect the strength and colour of the cement. (Taylor, 1964), Limestone with MgO not less than 3% precipitate impurities in the production of sugar (Khan and Akyar, 2004). Limestone from Kalambaina (1.58%), Kware (2.06%), Amanawa (1.42%) and Maiyama (1.38%) can be recommended.
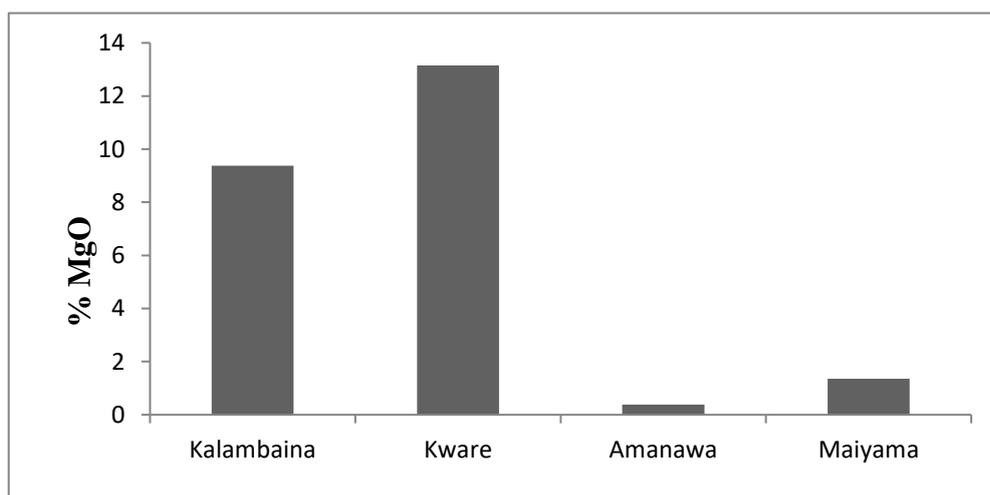

Figure 3: Composition of MgO in different samples determined using wet analysis

The percentage Fe_2O_3 in limestone used for cement production should be 3.3-4.6% (NIS, 2003). As shown in Table 1 the percentage composition of Fe_2O_3 using XRF analysis in limestone sample from Amanawa (7.43%) and Maiyama (9.53%) are above the range recommended by NIS (2003). Figure 4 presents the percentage composition of Fe_2O_3 using wet analysis in limestone samples of Kalambaina (4.99 %), Kware (6.51 %), Amanawa (6.82 %) and Maiyama (6.74 %). These values are not within the range recommended by NIS (2003). High Fe_2O_3 affect the strength of the cement (Hooton et al., 2007).The Fe_2O_3 content of samples from Kalambaina (3.26%) and Kware (4.34%) are within the range
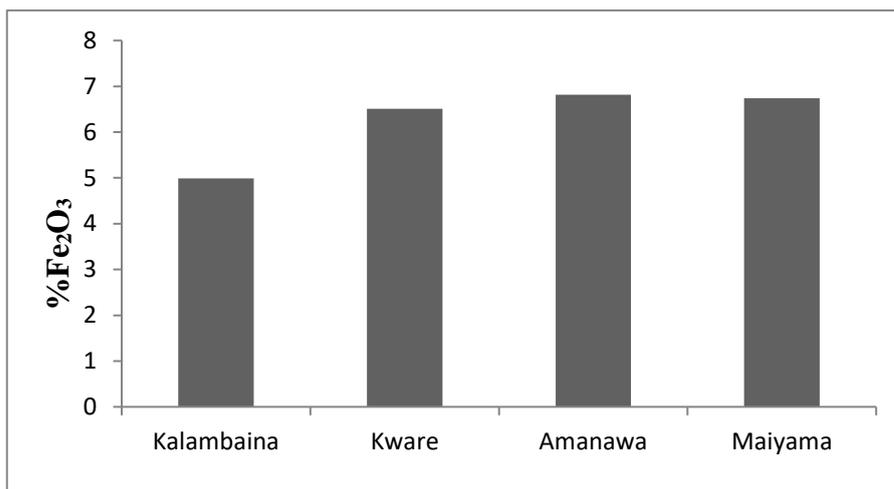
recommended by NIS (2003).

Figure 4: Composition of Fe_2O_3 in different samples determined using wet analysis

According to NIS (2003) the percentage Al_2O_3 in limestone used for cement production should be 3.0-6.4%. As presented in the Table 1 the percentage Al_2O_3 using XRF analysis in limestone sample from Kware (7.48%), Amanawa (15.78%) and Maiyama (20.52%) are above the range recommended by NIS (2003). Likewise, Kalambaina (4.99 %) value of alumina obtained in Figure 5 is within the range recommended by NIS (2003). Again, as shown in Figure 5 percentage composition for alumina using wet analysis in limestone sample from Kware (13.3%) Amanawa (10.02 %) and Maiyama (9.46 %) are higher than the range recommended by NIS (2003).   High Al_2O_3 content in limestone affects quality of cement for instance, it cause cracking of cement product (Hooton et al., 2007), On the other hand, the Al_2O_3 content of sample from Kalambaina (4.29%) is within the range recommended by NIS (2003) for cement production.
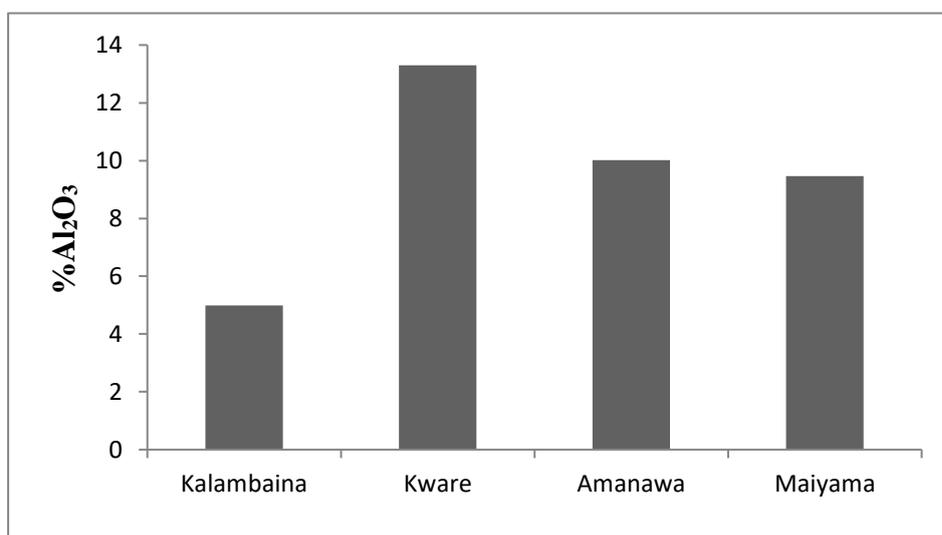

Figure 5: Composition of Al_2O_3 in different samples determined using wet analysis

The percentage SiO_2 in limestone used for cement production should be 14-16% (NIS, 2003). As shown in Table 1 the percentage composition of SiO_2 using XRF analysis in limestone samples from Kware (24.86%), Amanawa (41.50%) and Maiyama (48.40%) are above the range recommended by NIS (2003), On the other hand, the sample from Kalambaina (15.31%) is within the range recommended by NIS (2003) for cement production.

Figure 6 presents the percentage composition of SiO_2 using wet analysis in limestone samples of kalambaina (19.46 %), Kware (26.02 %), Amanawa (42.36 %) and Maiyama (49.94 %) are higher than the range recommended by NIS (2003). Limestone with at least more than 1% SiO_2 can be used for glass production (Khan and Akyar,2004), Limestone samples from Kalambaina (15.31%), Kware (24.86%), Amanawa (41.50%) and Maiyama (48.40%) can be recommended.
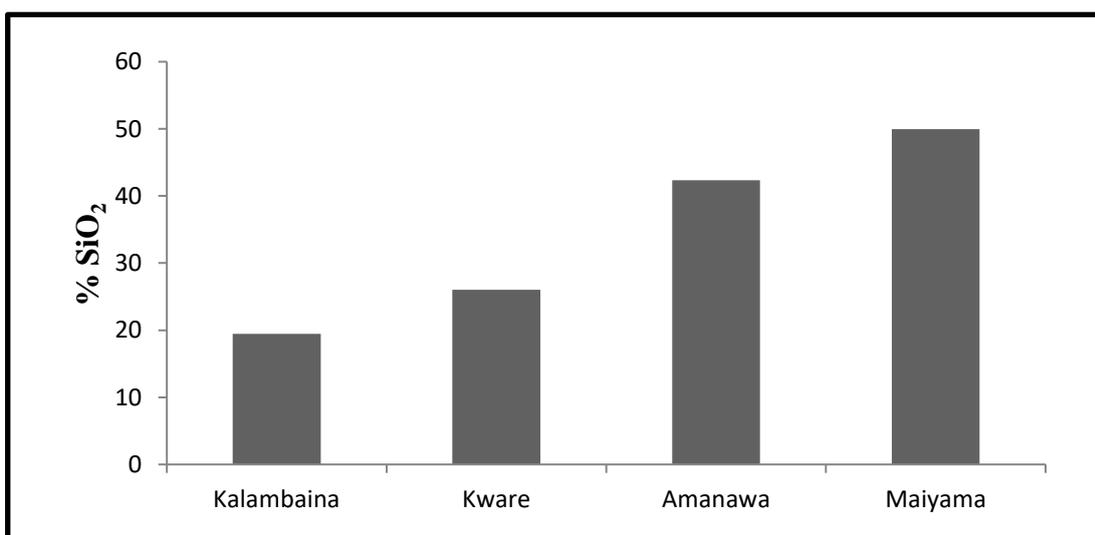

Figure 6: Composition of SiO_2 in different samples determined using wet analysis

According to NIS (2003) the percentage LOI in limestone used for cement production should be 40.38-40.86%. As shown in Table 1 the percentage composition of LOI using XRF analysis in limestone sample from Kalambaina (33.42%), Kware (28.43%), Amanawa (17.34%) and Maiyama (12.33%) are below the range recommended by NIS (2003).

Likewise, as shown in Figure 7 the percentage composition of LOI using wet analysis from samples kalambaina (33.01 %), Kware 928.01 %), Amanawa (17.43 %) and Maiyama (12.4 %) are lower than the range recommended by NIS (2003) and it affect a system for activating combustion in a combustion engine (Khan and Akyar,2004).
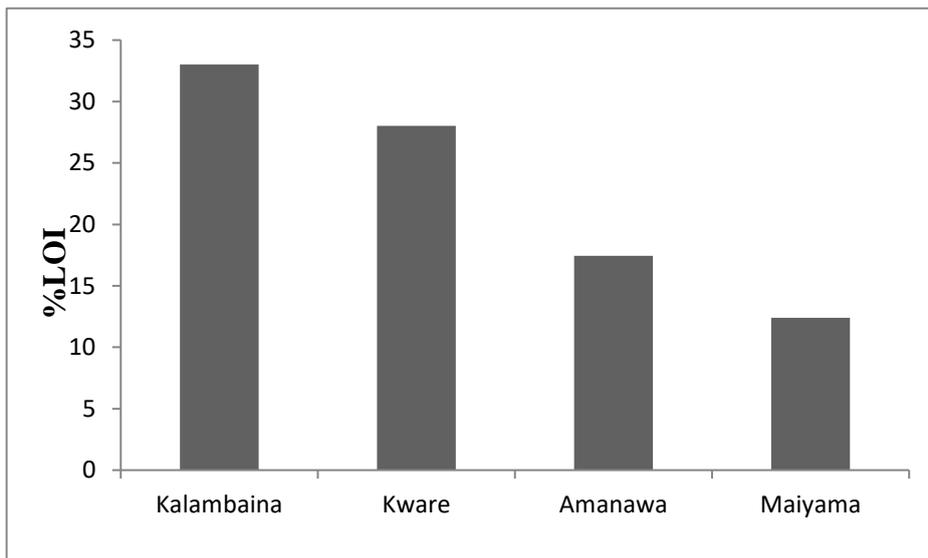
Figure 7: Composition of LOI in different samples determined using wet analysis

3.3. Composition of the Samples by AAS and FES

The result for the composition of samples (% wt) by AAS and FES (µg/g) are presented in table 2 below. According to (Ibrahim et al., 2012) chemical composition are naturally present in biological world in acceptable quantities but increase of these composition through anthropogenic contribution has since the last century been known to harm human and environment. Limestone is also associated with chemical composition as an evident in many studies conducted (Ahmed et al., 2009). However, chemical composition such as (Ca, Mg, Fe, Na and K) in limestone samples from Kalambaina, Kware, Maiyma and Amanawa in their oxide form are within the range and heavy metals such as (Cr, Cu and Pb) exceeded the maximum allowable concentration as recommended by WHO (WHO, 1990). Heavy metals are known to pose serious health problems to humans, affect plant growth and general damage to ecosystem (Bagudo et al., 2009).

Table 2. Composition of sample (% wt) by AAS and FES (µg/g)

Sample	CaO	S.D	MgO	S.D	Fe_2O_3	S.D	Cr_2O_3	S.D	CuO	S.D	PbO	S.D	Na_2O	S.D	K_2O	S.D
Kalambaina	32.64	0.11	3.51	0.04	2.78	0.03	0.05	0.01	0.012	0.05	0.37	0.02	5.84	0.06	17.26	0.08
Kware	29.16	0.10	4.52	0.06	2.51	0.04	0.06	0.004	0.005	0.01	0.35	0.02	8.44	0.07	9.74	0.07
Maiyama	18.16	0.07	17.36	0.07	2.91	0.04	0.03	0.01	0.032	0.07	0.36	0.02	6.45	0.06	15.77	0.08
Amanawa	12.74	0.07	7.59	0.06	2.59	0.03	0.05	0.01	0.02	0.08	0.33	0.02	6.75	0.07	13.56	0.07

3.4. Composition of the Samples by TGA/DTA

Gibbsite according to (Ralph *et al.,* 2011) shows an endothermic peak at about 200ºC – 300ºC. A TGA result shows these finding at 307.16ºC, 299.91ºC, 281.53ºC and 204.16ºC for Kalambaina,

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Kware, Amanawa and Maiyama respectively. The endothermic reaction corresponds to the hydration of the materials (Ralph et al., 2011). The % weight are listed in Table 3.

$$Al(OH)_3 \longrightarrow AlO(OH) + H_2O \quad \text{---} \quad [1]$$
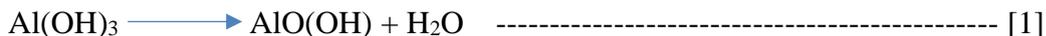
According to (Mogda et al., 1995) Kaolinite undergoes endothermic reaction at temperature of 380ºC – 700ºC. The TGA result shows these finding at 670.86ºC, 669.71ºC, 539.43ºC and 655.10ºC for Kalambaina, Kwara, Amanawa and Maiyama respectively. The endothermic reactions correspond to the hydration of the material (Mogda et al., 1995). The % weight are presented in Table 3.

$$Al_2O_3.2SiO_2. 2H_2O \longrightarrow Al_2O_3.2SiO_2+2H_2O \text{---------------------------------------} [2]$$

According to (Xiang et al., 2013), the decomposition of $CaCO_3$ occurs at 800ºC – 1000ºC. The curve TGA results show these finding at 853.36ºC, 827.01ºC, 796.12ºC and 845.10ºC for Kalambaina, Kware, Amanawa and Maiyama respectively. The endothermic reaction corresponds to the decomposition of the material. The % weight are shown in Table.3
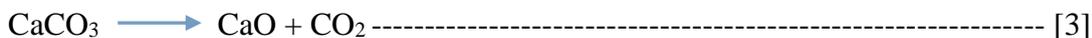
$$CaCO_3 \longrightarrow CaO + CO_2 \text{--} [3]$$

Table 3: Composition of the sample (%wt) by TGA/DTA

Parameter (% wt)	Kalambaina	Kware	Amanawa	Maiyama
Clay (gibbsite)	6.01	6.09	4.72	5.06
Clay (kaolinite)	4.83	4.80	2.89	4.80
$CaCO_3$	17.04	17.06	19.06	17.81
LOI	27.99	27.97	27.92	30.10

4. Conclusion

The present study shows that limestone samples from Kalambaina and Kware with $CaCO_3$ (76.50) and (56.09) respectively can be used for Portland cement. Although sample from Kware has magnesia content above the recommended limit while samples from Amanawa and Maiyama were found to have higher silica and alumina content which is advantageous in the formation of C_3S, C_2S, C_3A and C_4AF. Hence, limestone samples from Kalambaina, Kware, Amanawa and Maiyama can be used in the production of Portland cement. Limestone deposits from Kalambaina is the best followed by Kware, Maiyama and Amanawa.

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