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SUITABILITY OF THE LOW GRADE KALAMBAINA LIMESTONE DEPOSIT FOR GLASS MAKING

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Abstract: A study to determine suitability of the low grade Kalambaina limestone deposit for glass making has been carried out. Samples were collected from four different locations. The representative samples were analyzed and characterized to determine the chemical composition, mineral phase and microstructural morphology using X-ray fluorescence (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) respectively. The results of the XRF showed thatthe deposit consists of 45.66 wt% CaO, 0.38 wt% MgO, 0.35 wt% Fe_2O_3, 0.22 wt% Al_2O_3, 1.13 wt% SiO_2, 0.19 wt% TiO_2 and the amount of material lost on ignition was 42.99% (LOI). Qualitative and quantitative XRD analyses revealed that calcite was the dominant mineral followed by quartz which occurred as the lesser phase. The percentages of calcite and quartz in the sample were99.23 wt% and 0.77 wt% respectively. SEM/EDS analysis depicted the major elemental composition of thedeposit and then the SEM-micrograph demonstrated the spherical calcite dust as dominant phase. The composition of the limestone deposit compared favorably with standard except for high concentration of iron oxide (0.35 wt%) which is objectionable but the concentration of iron oxide is still tolerable for making green container glass (0.96 wt%). Notwithstanding, low grade Kalambaina limestone can be upgraded through beneficiation to minimize the iron oxide concentration.
Keywords: Limestone; Kalambaina; low grade; Glassmaking; River Sokoto

INTRODUCTION

Limestone is a vital industrial raw material used in glass, ceramics, cement, pharmaceuticals, bricks, paint and adhesive industries [1]. Limestone makes up 10% of the total volume of all sedimentary rocks and composed principally of calcium carbonate (calcite) or the double carbonate of calcium and magnesium (dolomite). It is commonly composed of tiny fossils, shell fragments and other fossilized debris and also limestone is usually gray, but it may be white, yellow or brown. It is a soft rock and is easily scratched and effervesces readily in any common acids [2,3].

In the manufacture of high quality glass, limestone should have a maximum of 0.004% Fe_2O_3 and above this value may be unpleasant because its presence even in minute amount tends to color the glass [4]. Lime is one of the major constituents of glass and is introduced in glass in three different forms namely; limestone or marble burnt lime and slake lime [5].

In glass industry, limestone is used in varying proportions from 2.0-18 wt% of the batch and its divalent calcium ion increases the strength of structure network and hence improves the chemical durability, inhibits cord formation, improves fusibility and also smoothness and luster among others [4, 6].

The addition of lime to glass batch ordinarily acts as flux towards sand and also improves viscosity which results in greater durability and resistance to weathering [5].

The aim of the study is to determine the suitability of Kalambaina limestone for glass making.

Kalambaina limestone deposit occurs two miles in width along the Southern valley of River Sokoto. The formation is composed of white to whitish gray chalky limestone with nodules of hard crystalline limestone at the lower part which is about 4.5m thick and constitutes about 80% calcium carbonate and above. It was noted that the upper 5 meters of the formation was dominantly loose gray clayey limestone [7, 2]. Table 1 presented the standard limestone specifications for glass making.

Table 1: Standard Limestone Specifications for Glass Making (Source:[8])

OXIDE	Wt%
SiO_2	<2.0
TiO_2	<0.1
Al_2O_3	<0.3
Fe_2O_3	<0.1
Mn_3O_4	<0.1
MgO	<3.0
CaO	>54.3
Na_2O	<0.1
K_2O	<0.1
P_2O_5	<0.1
SO_3	<0.5
Cr_2O_3	<0.1
SrO	<0.2
ZrO_2	<0.1
BaO	<0.1
NiO	<0.1
CuO	<0.1
ZnO	<0.1
PbO	<0.1
LOI	42.7
Total	100.0

The limestone for this study was sourced from Kalambaina limestone deposit in Wamakko local government area of Sokoto State, Nigeria.
Samples of about 5 kg of the Kalambaina limestone were collected from four different locations, crushed and sieved to about 75 µm particle size distributions from which a representative samples were taken by coning and quartering method for conduct of various analyses.

METHODS / CHARACTERIZATION OF SAMPLE USING ANALYTICAL TECHNIQUES

Representative samples were subjected to various analytical techniques to ascertained chemical composition, dominant mineral present in the sample and microstructural morphology using XRF, XRD and SEM respectively. In addition, a small portion of the fourth sample was dried at 100°C, roasted at 1000°C and then Loss on Ignition (LOI) was determined.
The first sample was subjected to XRF to determine oxides of calcium, magnesium, sodium, potassium, manganese, iron, aluminium, titanium, silicon, phosphorus, chromium, nickel, vanadium, zircon and copper.
The second sample was subjected to identification of dominant minerals by XRD using a back loading method and then the third and fourth samples were used to study surface morphology and loss on ignition respectively.

RESULTS AND DISCUSSIONS

Chemical composition of Kalambaina Limestone Deposit is illustrated in Table 2 while qualitative and quantitative XRD results are given in Figure 1 and Table 3 respectively.

Table 2: Chemical composition of low grade Kalambaina limestone deposit

OXIDE	Wt.%
SiO_2	1.13
CaO	45.66
MgO	0.38
Al_2O_3	0.22
Fe_2O_3	0.35
Cr_2O_3	<0.01
P_2O_5	0.04
V_2O_5	<0.01
TiO_2	0.01
Na_2O	<0.01
K_2O	<0.01
MnO	0.08
NiO	<0.01
ZrO_2	<0.01
CuO	<0.01
LOI	42.99
Total	90.85

The result in Table 2 demonstrates that low grade Kalambaina limestone has 45.66 wt% CaO (lime) content which was far below industrial limestone specification for making quality colourless glass (Aliyu et al, 2013). But, Kalambaina low grade limestone is higher than Indian Shahabad low grade limestone which has 43.2 wt% CaO [9]. Loss on ignition is within the acceptable level [8]. Similarly, Kalambaina low grade limestone contains low concentration of magnesia (0.38 wt%) when compared with the standard [8].
Apart from relatively high percentage of lime, it was detected that the sample contains 0.35wt% Fe_2O_3 which is unpleasant in glass making due to its colouring effect. Although, 0.96 wt% is tolerable for making green container glass [10]. However, Kalambaina low grade limestone can be upgraded to meet the requirements for soda-lime silica glass manufacture through beneficiation.
The qualitative and quantitative analyses result in Table 3 and Figure 1 have revealed the presence of calcite as dominant mineral followed by quartz as lesser phase. The percentage of calcite in the low grade Kalambaina limestone is 99.23 wt% and quartz is accounting for the balance.
The SEM/EDS analysis in Figure 2 shows the major elemental composition of the low grade Kalambaina limestone and the SEM- micrograph given in Figure 3 demonstrates the dominant spherical calcite dust alongside the lesser phase.

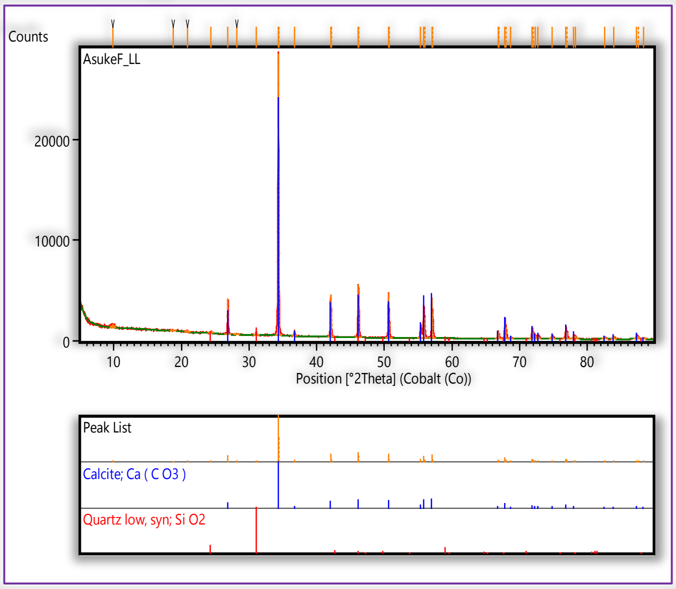

Figure 1: Qualitative XRD analysis of low grade Kalambaina limestone sample

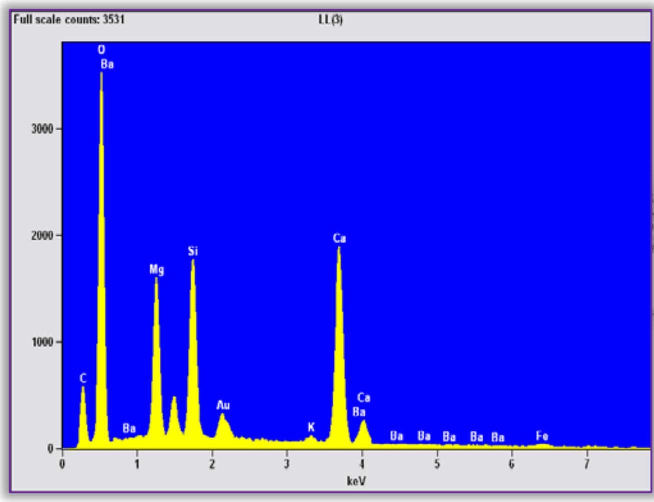

Figure 2: SEM/EDS analysis of low grade Kalambaina limestone

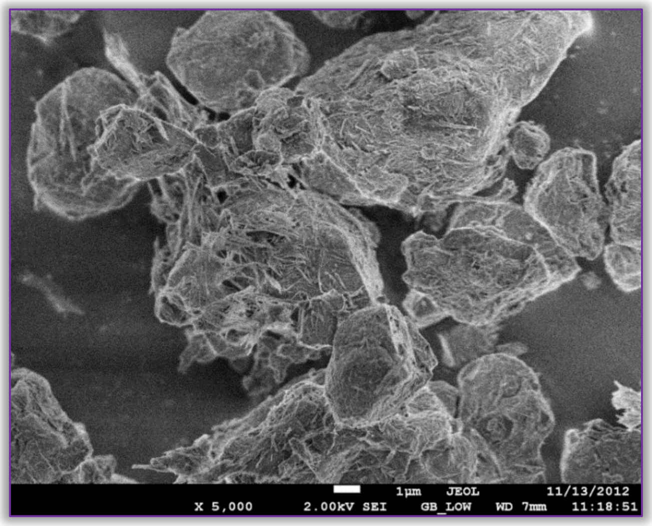

Figure 3: SEM-micrograph of low grade Kalambaina limestone sample at 5,000 Magnification Showing Spherical Calcite Dust.

Table 3: Results of quantitative XRD analysis of the low grade Kalambaina limestone sample

Mineral	Wt%	3α error
Calcite	99.23	0.17
Quartz	0.77	0.17

CONCLUSIONS

The low grade Kalambaina limestone has undergone instrumental analytical techniques and the results of the study revealed that it is suitable for making green container glass due to its relatively high calcite content and low iron oxide content.

Although, the sample can be upgraded by beneficiation to remove the iron oxide concentration so as to meet the industrial limestone requirements for making quality colourless glass.

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