CHARACTERIZATION OF TSAKASIMPTAH DOLOMITE AND ITS SUITABILITY FOR GLASS MAKING

[1]ALIYU Z. S. & [2]DAUDA M.
[1] Industrial Design Department Ahmadu Bello University, Zaria.
[2]Mechanical Engineering Department Ahmadu Bello University, Zaria

Abstract
The Tsakasimptah dolomite was subjected to instrumental analytical techniques to determine its suitability for direct use in glass making. The results of the XRF showed that the dolomite contains CaO-31.62%, MgO-12.75%, Fe_2O_3-0.63%, SiO_2-16.77%, Al_2O_3-1.74%,K_2O-0.17%, P_2O_5-0.09%, TiO_2-0.11%, MnO_2-0.02%, Na_2O -< 0.01%, Cr_2O_3- <0.01% , NiO_2-<0.01%, V_2O_5 - <0.01%, ZrO_2-<0.01%CuO-,0.01% and LOI-38.14%. The quantitative and qualitative XRD analyses of the samples revealed the presence of dolomite as the predominant mineral followed by calcite. The percentages of dolomite and calcite in the sample were 75.44% and 17.62% respectively. Although, SEM/EDX morphology shows the presence of dolomite characterized by clusters of massive rhombohedra microstructure and some slightly curved shape granular crystals. Also, the XRD has shown that both CaO-MgO have the highest peaks showing the presence of dolomite in high concentration. The CaO/MgO concentration has met the requirement for making soda-lime -silica and fiber glasses. Although It was detected that the sample contains 0.63% Fe_2O_3 which is far above the exploited dolomite range of 0.05% to 0.07% for industrial applications and also above the tolerable range of 0.025% for glass making. However, by beneficiation technique, the quality of the dolomite can be upgraded to meet the requirements of soda-lime silica glass and glass fibers industries.
Keywords (Characterization, Tsakasimptah, Dolomite, Glass making)

Introduction
Development of heavy and light industries increased the demand for dolomite as this material and its derivatives present great significance for various industries (Ahmad et al, 2013). Dolomite is an important sedimentary and metamorphic mineral found as the major mineral in dolostones and metadolostones, and key mineral in limestone and marbles where calcite is the predominant mineral present. Also found as a hydrothermal vein mineral forming crystals in cavities and found in serpentines and similar rocks. Dolomite is a carbonate mineral consists of calcium and magnesium carbonate ($CaCO_3$. $MgCO_3$) and has a theoretical composition of 45.65% and 54.35% for $MgCO_3$ and $CaCO_3$ respectively or 30.4% CaO and 21.9% MgO (Valentine, 1989). However, naturally, dolomite doesnôt exist in this exact p commercially, the rock containing 40-50% is magnesite ($MgCO_3$) and is usually called dolomite; it is classified under fluxing agents and construction minerals and is important for iron & steel and Ferro-alloys industries. Most if not all dolomite is a replacement of pre-existing limestone and this replacement process is known as dolomisation. The process is often incomplete and rocks termed ñdolomiteò are usually a c dolomite, dolomitic limestone and limestone. Most dolomite is formed from limestone by

replacement of some calcium ions by magnesium after deposition and the resultant dolomite mineral $CaMg(CO_3)_2$ is a true double salt, and calcium and magnesium ions in dolomite exist in crystal matrix(Valentine, 1989). In addition, dolomite has a calcium layer, then a carbonate layer, then a magnesium layer then a carbonate layer and so on. It is harder and denser than the calcite form of calcium carbonate or limestone and is more chemically inert and more impervious.

The limestone that is partially replaced by dolomite is referred to as dolomitic limestone, and there are two types of minerals often called dolomite, a true chemically uniform calcium magnesium carbonate with the chemically and a dolomitic limestone which is just an irregular mixture of calcium and magnesium carbonates(Ahmad, 2013). Dolomite deposits are therefore, usually associated with limestone. This fact, together with the presence of variable amount of impurities such as silica, sulphur, iron oxides and alumina has an important bearing on the suitability of dolomite for specific applications. For commercial purposes, the percentage should not go above 7% which makes it unsuitable for industrial use (Cardu et al, 2006)). It is then used only for road ballasts, building stones, flooring chips among others. Dolomite is a double carbonate of calcium and magnesium, $CaCO_3$. $MgCO_3$. It is of sedimentary origin and supposed to have been formed due to chemical action of sea-water containing high percentage of magnesia and limestone. The mineral dolomite crystallizes in trigonal rhombohedra system unlike calcite dolomite is a double carbonate having different structural configuration and does not dissolve rapidly or effervesce in acids unless it is scratched or in powdered form and is commonly characterizes by crystal twinning (Cardu et al, 2006).

Dolomite is an essential raw material for float glass and fiber glass making, and there is normally no economic alternative. The major advantage of dolomite as a raw material is that it is relatively cheap (BGS, 2006), other applications include; steelmaking industry as a flux and for manufacture of refractories for basic open hearth furnaces, Bessemer converters and steel ladles. In the cement industry, it is used in refractories which line rotary cement kilns, also has agricultural applications as a fertilizer, soil conditioner and stock feed supplement among others. In glassmaking, it is added to raw material mixture in the form of dolomite grits (-1 mm) as one of the essential components for the input of glass modifiers that is CaO and MgO. In most cases, dolomite exploited in dolomite exploited in quarries does not satisfy demanding specifications because impurity like Fe_2O_3 is very objectionable, and its content in exploited dolomite before beneficiation varies in range from 0.052% to 0.07% (Cardu et al, 2006).

Glass grade dolomite is paramount and is typified by its purity and consistency in which the MgO and CaO content should not differ by more than 0.5%. The chief objectionable impurities include oxides of iron, chromium, vanadium, manganese, and lead all of which colour glass or cause defects in the glass. Dolomite with iron oxide contents of less than 0.025% Fe_2O_3 is required in glass industry for the manufacture of colourless glass containers and sometimes low iron float glass (BGS, 2006 and Shelby,2005).

Apart from glass industry, dolomite has a wide range of applications, the most important of which by volume is in construction, where it may substitute for limestone. However, for non construction purposes where its chemical properties or degree of whiteness are significant. The MgO content of dolomite is commonly expressed after calcination. Pure dolomite has an MgO content of about 40%. However, glass industries normally use pre-calcined MgO content for control purposes and there is a theoretical maximum of about 21.8% MgO (BGS, 2006).

Dolomite after calcination is used for refractory purposes in the lining of furnaces like basic open-hearth steel furnaces and basic Bessemer converters. It is also used as flux in iron, steel, ferroalloys and for the production of carbon (IV) oxide required for the manufacture of beverages. There has been considerable interest in recent years in the characterization of various mineral deposits for industrial consumption. The present study deals with the characterization of Tsakasimptah dolomite deposit for glass making.

Methodology:

Materials and Methods

Dolomite was obtained from Tsakasimptah in Adamawa state and the crushing process of the sample was achieved using crusher machine then sieved using > 100 mesh to obtain dolomite powder. The sample was dried at 100°C and roasted at 1000°C to determine Loss on Ignition (LOI). Then, 1g sample was mixed with 6g lithium tetra borate flux and fused at 1050°C to make stable formula for trace element analyses and then the sample was mixed with a PVA binder and pressed into pellet using Thermo Fisher ARL9400XP plus Sequential with WinXRF software. The sample was analyzed for silica, lime, loss on ignition and oxides of sodium, potassium, magnesium, phosphorus, manganese, titanium, iron, copper, chromium, nickel, zirconium, vanadium among others.

Scanning Electron Microscopy equipped with an energy dispersive spectrometer (FESEM/EDS) model number JEOL JSM 7500F was used to examine the microstructure. A small quantity of the sample was placed on the sample holder and then transfer into the machine in which a vacuum was increased in the machine chamber. The sample was irradiated to produce emission that was translated to a micrograph for morphological identification.

Similarly, identification of crystalline phases was carried out by XRD using a back loading technique which required preparation of fresh samples. The samples were analyzed using a PAN analytical XôPert Pro diffractometer with xôcelera variable divergence and receiving slits with Fe filtered Co-KŬ radiation.

The various phases formed were determined using Xô Pert High score plus phases identified are shown in the graphical representations. The Rietveld technique (Autoquan program) was used to estimate the relative phases amount in weight %, and errors are on the 3 sigma level in the column to the right of the amount. The quantification did not take cognizance of amorphous phases present. Figure 1 and table 2 have shown qualitative and quantitative results of the samples respectively.

Results and Discussion

The chemical composition of Tsakasimptah Dolomite Deposit using XRF is given in table 1 while qualitative and quantitative XRD results are presented in figure 1 and table 2 respectively.

The 31.62% CaO, 12.75% and MgO contents of the Tsakasimptah dolomite did not fall within the range of 21.9% MgO and 30.04%CaO (Valentine, 1989) for industrial applications. However, Tsakasimptah dolomite has met the CaO and MgO requirement for common commercial soda-lime-silica glasses such as windows (MgO-4% & CaO-9%), containers (MgO-0.2% & CaO-11%), incandescent lamps(MgO-4% & CaO-3%) (Shelby, 2005) as well as the CaO and MgO requirement for common glass fibers wool (MgO,0-5% & CaO,5-13%), E-glass(MgO, 0-5% & CaO, 16.25%) and C-glass (MgO, 2-4% & CaO, 11-15%) among others (Shelby, 2005). Apart from the high percentage of $CaMg(CO_2)_3$, it was revealed that the sample contains about 0.63% Fe_2O_3 which is objectionable due to its colouring effect. Iron oxide (Fe_2O_3) is the major challenge of the Tsakasimptah dolomite sample simply because its concentration is high up to 0.63%. For this reason, there is need to upgrade Tsakasimptah dolomite to

glass making grade through beneficiation of the iron oxide. The qualitative and quantitative XRD analyses results in figure 1 and table 2 had suggested that dolomite was the predominant mineral in the sample followed by secondary minerals like calcite, quartz and then plagioclase. The percentages of the dolomite, calcite, quartz and plagioclase are 75.44%, 17.62%, 4.13% and 2.81% respectively. Figure 2 reveals that Ca/Mg has the highest peak indicating the presence of CaO/MgO in high concentration while SEM/EDS analysis given in plates 1-6 suggested the presence of dolomite characterized by clusters of massive rhombohedra crystals in which some have slightly curved shape. In addition, the concentration of CaO and MgO of Tsakasimptah dolomite is higher than those of Oreke dolomite deposit as it contains CaO-10% and MgO-6.4% also suitable for making common soda-lime-silica glass (Akande et al, 2012).

Conclusion

The present study showed a successful characterization of the Tsakasimptah Dolomite and the result has revealed that the deposit is suitable for making a wide spectrum of commercial glasses such as containers, windows, incandescence lamps as well as glass fibers. The dolomite is rich in calcite 31.62% and magnesia 12.75% and both of them play significant role in glass making as each is a stabilizing agent providing chemical stability, chemical durability and some mechanical properties such as hardness. Although, the dolomite has a relatively low iron oxide content 0.63%. But, dolomite for making colourless glass should contain less than 0.03% Fe_2O_3 (BGS,2006). Therefore, Tsakasimptah dolomite deposit should undergo beneficiation so as to upgrade it for making high quality colourless glass.

Table 1: Chemical Composition of Tsakasimptah Dolomite determined by XRF

Dolomite Composition	Weight %
SiO_2	16.77
TiO_2	0.11
Al_2O_3	1.71
Fe_2O_3	0.63
MnO_2	0.02
MgO	12.75
CaO	31.62
Na_2O	0.01
K_2O	0.17
P_2O_5	0.09
Cr_2O_3	0.01
NiO_2	0.01
V_2O_5	0.01
ZrO_2	0.01
CuO	0.01
LOI	38.14
Total	101.99

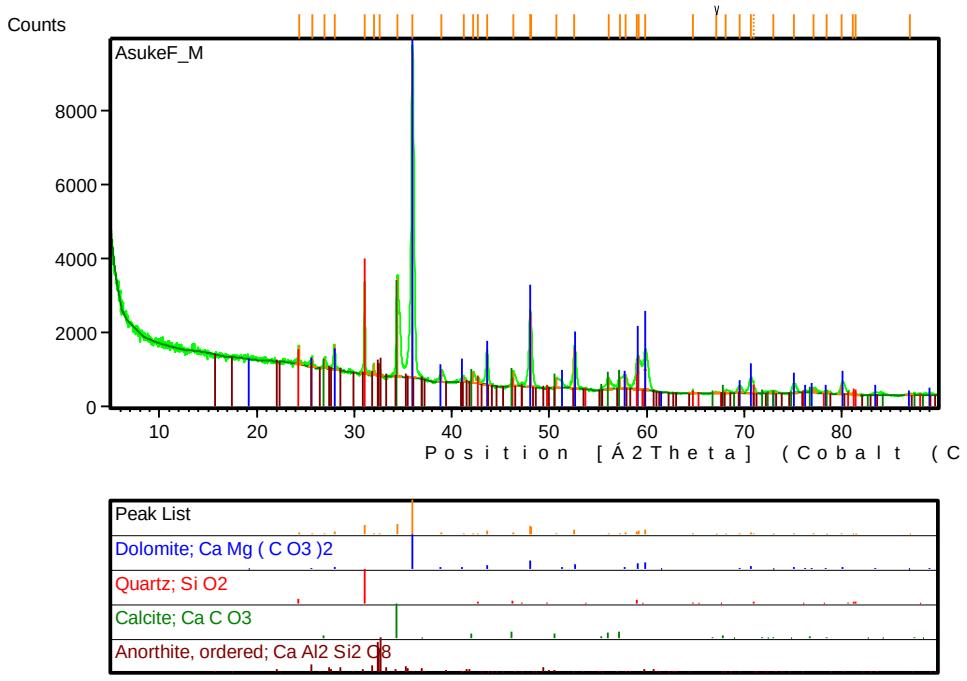

Figure 1: Qualitative Analysis of Tsakasimptah dolomite Sample

	Wt %
Calcite	17.62
Dolomite	75.44
Plagioclase	2.81
Quartz	4.13

Table 2: Results of Quantitative XRD Analysis of Tsakasimptah dolomite Sample

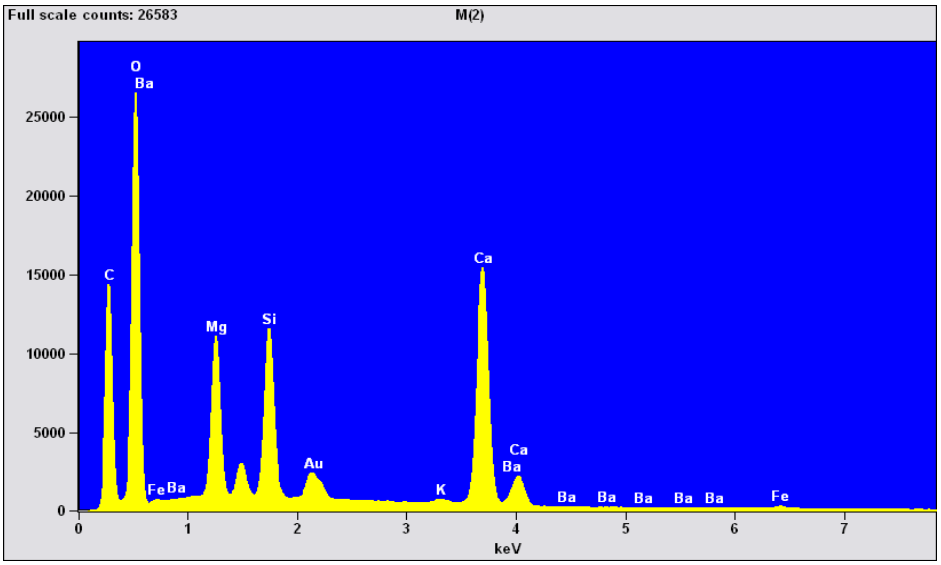

Figure2: SEM/EDX Analysis of the Tsakasimptah Dolomite Sample

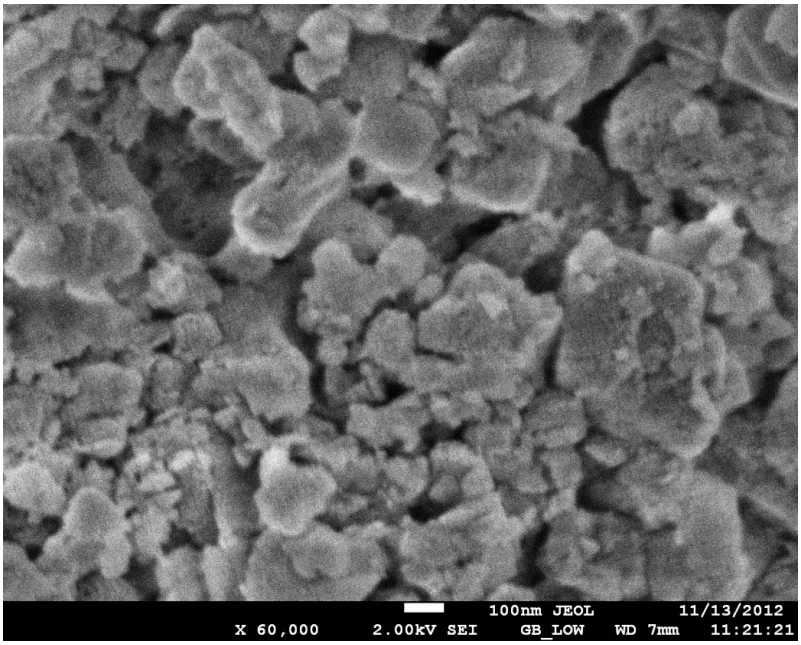

Plate 1: Morphology of Tsakasimptah dolomite at 60,000 magnifications
Showing clusters of rhombic curved face granular crystals.

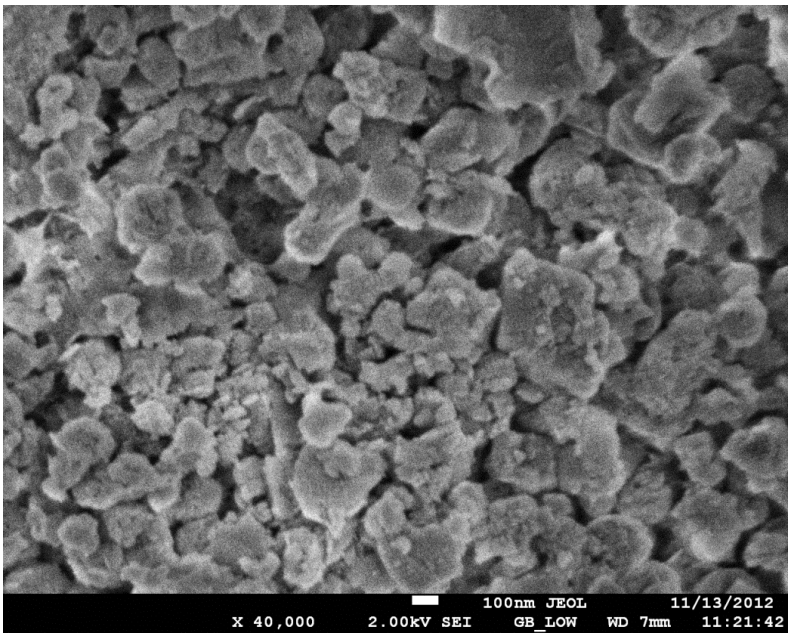

Plate 2: Morphology of Tsakasimptah dolomite at 40,000 magnifications showing clusters of massive rhombohedra and slightly curved granular crystals

.

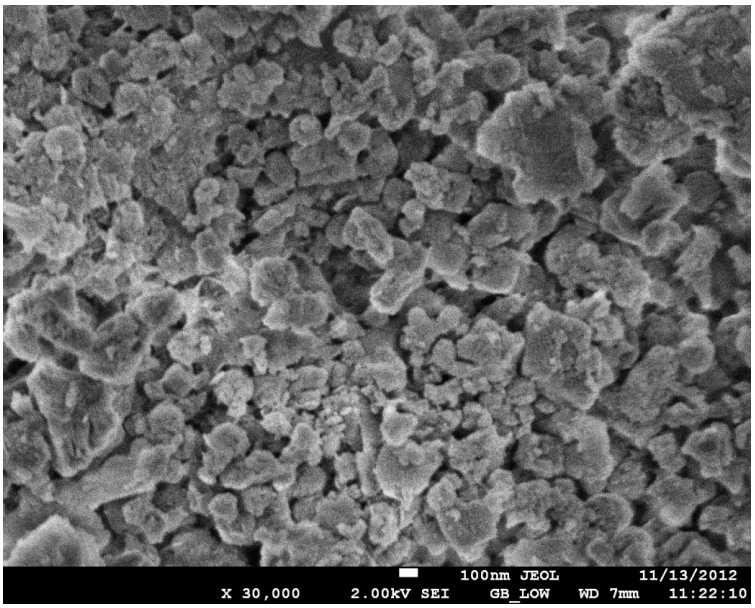

Plate 3: Morphology of Tsakasimptah dolomite at 30,000 magnifications showing clusters of rhombohedra twins and simple rhombs with slightly curved faces.



Plate 4: Morphology of Tsakasimptah dolomite at 20,000 magnifications showing clusters of massive rhombohedra granular crystals.

Plate 5: Morphology of Tsakasimptah dolomite at 10,000 magnifications Showing large clustered blockage of massive granular crystals.