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Research Article

CHARACTERIZATION OF ASHAKA LIMESTONE FOR POTENTIAL DIVERSIFICATION OF ITS APPLICATIONS

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ABSTRACT

This study is on the characterization of Ashaka limestone for potential diversification of its applications. The analyses were performed on finely ground sample of the limestone. X-ray Fluorescence spectroscopy was used to determine the chemical compositions of the limestone. Its mineralogical composition was determined by X-ray Diffractometer (XRD). Size analysis of the limestone was carried out, and scanning electron microscope, (SEM) was used to study the surface morphology of the sample. Analyses of the results revealed that Ashaka limestone has CaO (66.9%) as the predominant constituent in respect of chemical composition, and calcite as the major mineral. Density Functional Theory (DFT) cumulative surface area of the limestone is 1.041 X/g. Langmuir method of size analysis grossly estimated the surface area, while DFT method yields reliable surface area and pore volume measurements. The DFT adequately accounted for the effects of microporocity. The surface morphology of the limestone sample showed that the particles are packed together in powdered form with visible pores that will allow passage of fluids. Ashaka limestone is a potential source of acidic soil ameliorant. Thus, besides using it for cement production, it should be diversified into its application in agriculture (in terms of acidic soil amelioration).

Keywords: DFT, CaO, Ashaka limestone, calcite.

INTRODUCTION

According to Ofulume *et al.,* 2018, limestone is a sedimentary rock composed primarily of Calcium Carbonate ($CaCO_3$). Various limestones differ considerably in their chemical compositions and physical structure. High calcium limestone is composed primarily of the minerals calcite or Aragonite ($CaCO_3$) with a total oxide (CaO + MgO) content of not less than 95 %. It can be a fine to a coarse stone with varied porosity and hardness. As a form of limestone, chalk is soft, fine rained, and highly porous. Dolomitic and magnesian limestones, in addition to the $CaCO_3$, contain a relatively large proportion of $MgCO_3$. Usually limestones containing 20% to 44% $MgCO_3$ are referred to as dolomite or as dolomitic limestone, and those containing between 5-20 % $MgCO_3$, as magnesian limestone. Leontakianakos *et al.,* 2010 stated that limestones and their varieties represent the most frequently used rocks in industry and are included among the thirty most important raw materials. Though limestone varied in quality, it is an exceptionally valuable raw material for construction and cement industries. Nigeria is blessed with abundance of mineral resources and they have availability of limestone spread throughout the States of the country. The limestone deposits in these locations are rich in calcite which can be useful in production of cement, in agriculture and in chemical/industrial uses (Penuel *et al.,* 2015). Ashaka is popular for limestone deposit. It is a town located in Funakaye Local Government Area of Gombe State, Nigeria. This deposit is not adequately tapped because of poor technological practice. Physical characteristics of limestone play an important role in evaluation of a deposit. Ofulume *et al.,* (2017) asserted that crystal structure and physical characteristics of the various limestone's determine the quality of the lime product. Certain physical properties of limestone (such as coarse crystallinity, friability, micro fracturing, highly porous and thin-bedded structure) may indicate general susceptibility to decrepitation during calcination (Kilic, 2014). The texture of the limestone is a factor in the successful calcination of the stone into lumps of lime. Coarse grained limestone's are prone to fracturing and crumbling into fines when heated. They can be disintegrated to dust by the heat of the calcination process, a situation dreaded by lime manufacturers. But, fine grained limestones can easily be calcined to form lumps of lime because of resistance of crystals to temperature stress. The physical properties of limestone rock are vital in determining its texture and applications. The chemical analysis of a carbonate rock is essential for estimating the neutralizing value of agricultural limestone, which is usually expressed in terms of calcium carbonate equivalent (CCE). The calcium carbonate content (% $CaCO_3$) of the limestone ranges from 65.08 to 82.41% (Ofulume *et al.,* 2018). Chemical compositions of limestone determine its reactivity. Chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silica, iron, magnesium, manganese, sodium, and potassium (Kilic, 2014). The aim of this study is to characterize Ashaka limestone for potential diversification of its applications. The specific objectives of the study are to determine; the chemical compositions, mineralogical characteristics and surface morphology of the limestone.

MATERIALS AND METHODS

Determination of Chemical Composition

X-ray Fluorescence spectroscopy (supreme 8000, oxford instrument) was used to determine the chemical compositions of the limestone. The sample cup was assembled using oxford instruments Poly-M XRF sample film. The powdered sample was pressed in the cups using a set of dies and a press machine. Then, the cup containing the sample was placed on the auto–sampler using safety window, which is provided in case of sample leakage. After placing the sample on the instrument tray and entering the identification and position at the integrated keypad, measurement was started by pressing the start

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button. The samples were irradiated with high energy x-rays from the controlled x-ray tube. After the first few seconds of measurements, live result was displayed; allowing a rapid assessment of product quality to be made. The result was continually updated till the end of the measurements. XRF peaks with varying intensities were created and were present in the spectrum (a graphical representation of x-ray intensity as a function of peaks).

Determination of Mineralogical Composition

Mineralogical composition of the limestone sample was determined by X-ray Diffractometer (XRD). The XRD analysis was performed on finely ground sample of the limestone. The X-ray diffraction pattern was taken using Empyrean Pan Analytical. The powdered samples of the limestone was prepared by preparation block and compressed in the flat sample holder to create a flat smooth surface that was later mounted on the sample stage in the XRD cabinet. The sample was analyzed using reflection transmission spinner stage using the theta-theta (X-ray beams at certain angles of incidence) settings. Two-theta (2Θ) starting position was 4 degrees and ends at 75 degrees with a two–theta step of 0.026261 at 8.67 seconds per step. Tube current was 40mA and the tension was 45VA. A programmable divergent ship was used with width mask.

Size Analyses of the Samples

Size analysis of the limestone was carried out by standard method (Francisco et al, 2018). The sample was placed in a sample cell. The filled sample cell bulb was inserted into the heating mantle. Clamp was placed around the mantle so that the sample cell is held firm. The sample cell stem was inserted into the sample preparation station. It was secured in the preparation station by tightening the knurled ring. Then, out gassing by entering the control panel menu was initiated. The out gassing temperature was set at 300 ^{o}C, the system was switched on the heater and instructed to start degassing. For the sample analysis, the Dewater was filled to the internal upper mark with liquid nitrogen. Then the sample cell containing an out gassed sample was placed into the analysis station. All selections on the start analysis sample menu were completed. After completing all the fields on the start analysis menu, the analysis started by clicking the start button.

Determination of Surface Morphology of the Samples

Scanning electron microscope, (Phenom pro x-ray, phenom world Emdhoven Netherlands) was used to study the surface morphology of the sample. It is a type of electron microscope that produces images of a sample by scanning the surface with focused bean of electrons. The electrons interact with atoms in the sample producing various signals that contain information about the samples surface topography and composition. The electron beam was scanned in a raster scan pattern, and the beam position was combined with the detected signal to produce an image. The Sample was placed on double adhesive which was on a sample stub, was coated sputter coater by quorum technologies model Q150R, with 5nm of gold. Thereafter it was taken to the chamber of SEM machine where it was viewed via NaVCaM for focusing and little adjustment, it was then transferred to SEM mode, was focused and brightness contrasting was automatically adjusted, afterward the morphologies of different magnification was store in a USB stick.

RESULTS AND DISCUSSION

Chemical Compositions of the Limestone

Chemical compositions of Ashaka limestone was obtained through the XRF analysis. The analyte concentration of the limestone is presented in Table1. It revealed the constituents as CaO (66.9%), SiO_2 (18.4%), Al_2SO_3 (6.9%), Fe_2O_3 (4.0%), SO_3 (0.8%), MgO (0.7%), TiO_2 (0.6), and traces of Mn_2O_3, SrO, K_2O, Cl, P_2O_5, Cr_2O_3 and ZnO. Chemical composition of limestone determines its application (Kilic, 2014; Ofulume *et al.,* 2018). Recorded high CaO content indicate that besides using Ashaka limestone for cement production, it is a potential source of acidic soil ameliorants.

Table 1: Analyte concentration of Ashaka limestone

Element	Concentration
Na2O	0.000 Wt %
MgO	0.723 Wt %
Al2O3	6.852 Wt %
SiO2	18.367 Wt %
P2O5	0.265 Wt %
SO3	0.836 Wt %
Cl	0.091 Wt %
K2O	0.905 Wt %
CaO	66.852 Wt %
TiO2	0.612 Wt %
Cr2O3	0.004 Wt %
Mn2O3	0.411 Wt %
Fe2O3	4.012 Wt %
ZnO	0.003 Wt %
SrO	0.069 Wt %

Mineralogical Compositions of the Limestone

The mineralogical composition of Ashaka limestone as determined by XRD is shown in Figure 1. It revealed that Ashaka limestone is made up three minerals (calcite, kaolinite and quartz) in the order of calcite > kaolinite > quartz. It is predominantly a calcite-type of limestone. This shows that Ashaka limestone can be used for agricultural purpose; agricultural lime for acidic soil amelioration (Guemmadi *et al.,* 2009; Penuel *et al.,* 2015; Akinniyi and Ola, 2016).

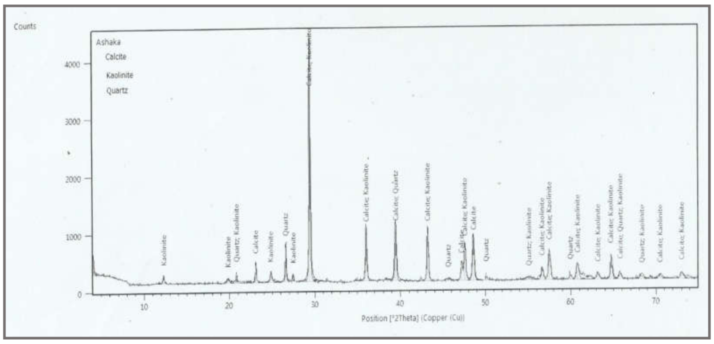

Figure 1: Mineralogical Compositions of the Ashaka Limestone

Size Analysis of the Limestone

Size analysis (surface area data, pore volume data and pore size data) of the Ashaka limestone sample is presented in Table 2. DFT cumulative surface areas of Ashaka limestone is 1.041 X$10^2 m^2$/g. The Density Functional Theory (DFT) helps to distinguish between different pore structural morphologies, to account for the effects of microporocity, and to predict the pore sizes (Landers et al, 2013). It is applied for the determination of pore size distribution from adsorption isotherms. Langmuir method grossly estimated the surface area, while DFT method yields reliable surface area and pore volume measurements. This observation is in agreement with the finding of previous work (Occelli *et al.,* 2003). The parameters from the DFT methods are vital as a result of its rigorous theoretical basis that covers the whole region of micro- and mesopores and provides an opportunity of customization to different adsorbates, materials and pore morphologies (Landers *et al.,* 2013). The DFT is adequate for the characterization of micro- and mesoporous materials of various origins. It introduces the surface roughness as additional structural parameter characterizing the pore wall heterogeneity.

Table 2: Size Analysis of Ashaka Limestone

Analysis	Surface Area Data
Langmuir surface area	2.022 x $10^3 \mathrm{m}^2$/g
DFT cumulative surface area	1.041 x $10^2 \mathrm{m}^2$/g
	Pore Volume Data
DFT method cumulative pore volume	1.252 x 10^1cc/g
	Pore Size Data
DFT pore Diameter (Mode)	2.647nm

SEM Analysis of the Limestone

The scanning electron microscopic analysis of Ashaka limestone is shown in Figure 1. The scanning electron microscope (SEM) produced the image of the limestone sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The surface morphology of the limestone was revealed. The micrograph showed that the particles are packed together in powdered form with visible pores that will allow passage of fluids. The presence of such pores is an indication that there will be effective removal of CO_2 during the calcination process, and subsequent improvement of the CaO yield (Maina 2013; Nurfatirah *et al.,* 2015).

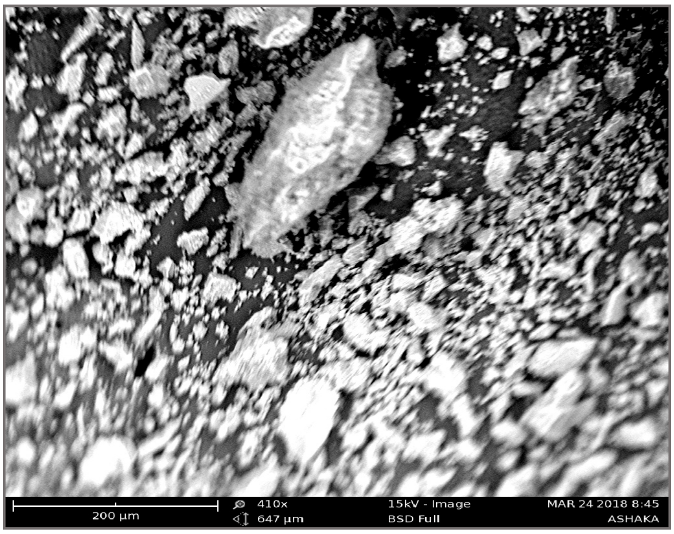

Figure 2: SEM Analysis of Ashaka Limestone

CONCLUSION

From the analyses of the experimental results, the following conclusion can be made: As obtained by the XRF analysis, CaO is the predominant constituent in respect of chemical composition of the limestone sample. The XRD analysis revealed calcite as the major mineral of the limestone. The surface morphology of the limestone sample showed that the particles are packed together in powdered form with visible pores that will allow passage of fluids. Langmuir method of size analysis grossly estimated the surface area, while Density Functional Theory (DFT) method yields reliable surface area and pore volume measurements. The DFT adequately accounted for the effects of microporocity. Ashaka lime is a potential source of acidic soil ameliorant.

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