Chemistry Research Journal, 2023, 8(3):35-44
Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Physico-chemical Characterization of Calcitic Marble from Idadjo (Ouèssè) in Benin Republic

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Abstract The objective of this study was to valorize the natural resources located in the Republic of Benin, in particular, marble obtained from Idadjo (Ouèssè). It was characterized to elucidate its properties for industrial applications. The results of the analysis by X-ray diffraction, infrared spectroscopy, chemical analysis by X-ray fluorescence and thermal analysis showed that the marble of Idadjo is pure calcite. This marble sample is very white and basic with pH ≈ 8.5. The particle size analysis of the powder particles of this marble showed two major size fractions: 34 % of the particles have a size between 250 µm and 500 µm and 23 % of the particles have a size between 125 µm and 250 µm. These characteristics make this marble very good additive that can be used in the production of mortar and concrete. The results also show that the Idadjo marble is a rich source of calcium carbonate and can be used as a precursor for the production of apatite, gypsum and its derivatives.

Keywords marble; characterization; calcite; apatite; gypsum

1. Introduction

Marble is a very common building material [1][2]. The major phases constituting marble are either calcite ($CaCO_3$), or dolomite [$CaMg(CO_3)_2$] or both when they coexist in chemical equilibrium [3][4][5]. Marble has been widely used as a raw material for the illustration of works of art [5].

Some recent studies carried out by Topcu et al. [6], Alyamac and Ince [7] showed that four different marble dusts produced in Turkey could be successfully and economically utilized as fillers in self-compacting concrete. Corinaldesi et al. [8], reported that marble powder proved to be very effective in assuring very good cohesiveness of mortar and concrete [8][9][10], even in the presence of a superplasticizing admixture [11], provided that water to cement ratio was adequately low.

Powdered marble can also be used as calcium and magnesium-based adsorbents for pollutants removal from drinking water, such as fluoride ions [12][13][14][15][16], heavy metals ions [17][18][19][20][21][22][23][24][25][26][27], and methylene blue [28][29].

According to OBRGM (Office Béninois des Recherches Géologiques et Minières) [30], the Idadjo marble deposit is estimated at around 6 million tons (just a small prospection). From available literature, studies have mainly been concentrated on the thermophysical properties of granite, marble and basalt deposits in Benin. They reported that granite is more insulating whiles marble has better ability to store heat [31]; however, no physicochemical

characterization of the marble was undertaken. The physical and chemical properties of natural stones play an important role in choosing their field of application especially as building stone.

This study carefully presents the results of the physicochemical characterization of marble sample taken from Idadjo in Benin Republic in order to demonstrate its different potential applications. X-ray diffraction analysis, granulometric study, thermal analysis, chemical analysis by X-ray fluorescence and infrared spectroscopy have been used to characterize this sample for its physical, thermal, chemical and microstructural properties.

2. Materials and Methods

2.1 The Study Area and Sample Collection

The marble sample was collected from deposit site of Idadjo (Ouèssè) in Benin. Information on the sample collected and the sampling areas are presented in Table 1 and Fig 1 respectively.

Table 1: The names of the village, municipality, department, and code of the sample studied.

Department	Municipality	Village	Sample code
COLLINES	Ouèssè	Idadjo	IDA

After the sample collection in marble deposit site, the primary marble blocks were coarsely crushed into secondary marble blocks and taken to the laboratory for further evaluations.

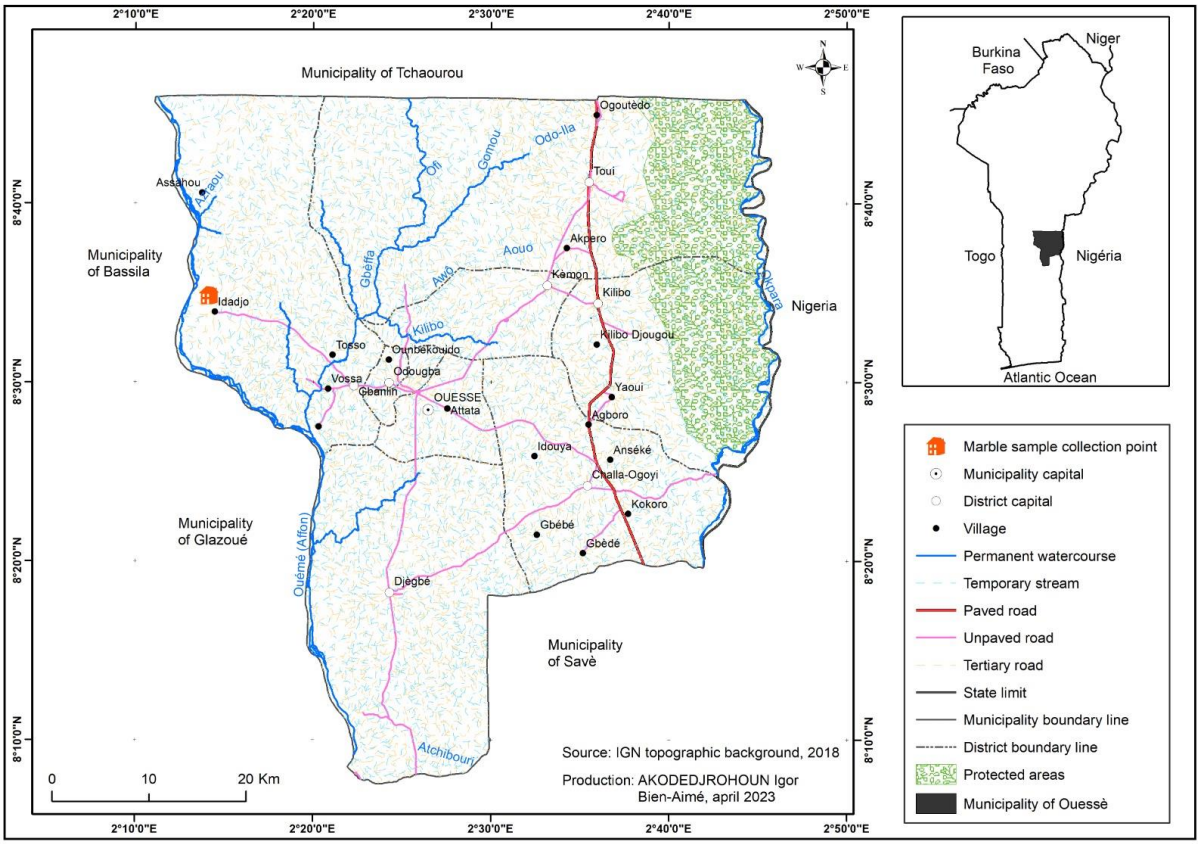

Figure 1: Map of Benin showing sample location

These secondary marble blocks were further crushed into coarse marble particles (aggregates) using a mass hammer mill to facilitate crushing: this is known as secondary crushing. These obtained marble particles were plundered in an aluminum mortar and then finely ground in a ceramic mortar. The marble powder obtained was sifted through a 500 micrometers mesh sieve. The sifted marble powder (*see Fig 2*) was stored at room temperature in clean plastic bottles.

Figure 2: Pictures of marble and powder obtained after crushing

2.2 Methods

For the granulometric analysis, about 200 g of marble powder sample was sieved and separated into six different fractions by using Haver & Boecker sieves with mesh sizes ranging from 500 µm to 50 µm. With the aid of a Mettler-Toledo pH-meter, the pH of sample was determined according to the method used by Emofurieta et al [32]. Typically, 5 g each of crude marble powder was placed in two s 50 mL bottle of distilled water and magnetically stirred for 24 h and 48 h respectively. After this time, the colloidal solution was left standing for 12 hours to allow the settling of the marble suspensions; after which the pH measurement was performed on water supernatants [33]. Five separate tests were carried out and the average values taken.

The percentage mass of calcium carbonate in the powdered marble sample were measured using the back titration methodology.1 g of each powdered marble sample was weighed and placed in labelled 250 mL conical flasks. Few drops of ethanol were added to the flasks to act as a wetting agent and catalyst for acid reactions. 50 mL of HCl solution (1.0 M) was then added to each of the labeled conical flasks, and swirled well to completely wet all the solids. The solutions in the flasks were magnetically stirred for 5 hours to allow the total dissolution of the carbonate ($CaCO_3$) contained in the powder according to the reaction showed in equation (1).

$$CaCO_3 + 2(H_3O^+ + Cl^-) \rightarrow (Ca^{2+} + 2Cl^-) + CO_2 + 3H_2O. \quad (1)$$

3-4 drops of phenolphthalein indicator were added to the flasks, whiles excess of unreacted acid was titrated against standardized NaOH solution (2 M), until barely pink color appears, persists for 30 s and fades slowly. The titration experiments were repeated 5 times to obtain concordant values. The mass percent of calcium carbonate in the powdered marble samples was determined using equation (2)

$$\%(CaCO_3) =. \frac{\mathrm{m}(CaCO_3)}{\mathrm{m(marble\ powder)}} x\ 100 \quad (2)$$

X-ray powder diffraction (p-XRD) measurements were performed using a Philips diffractometer (PANalytical, X'pert Pro MPD model) with a Bragg-Brentano configuration equipped with a Cu-Kα radiation (1.54059 Å) tube operated at a voltage of 45 kV and current of 40 mA. The data of the randomly arranged powder sample were collected in the 5 °- 80 ° 2θ value range with scan speed of 0.042°/sec, step size of 0.01°and a count time of 10.0 s per step. The diffraction patterns were matched against the ICDD's PDF database and qualitative phase analysis conducted using the X'Pert Highscore plus search match software (Panalytical, Netherlands).

The chemical composition of the marble sample was determined using a THERMOFISHER ARL PERFORM'X 2.5KW X-ray fluorescence spectrometer. The sample studied was analyzed in the form of pellets. Thus, 2 g of very fine powder are shaped into a uniform pellet with a diameter of 25 mm using a mold under a pressure of 8 to 15 tons.

Chemical bonding was analyzed by transmission infrared spectroscopy, using a Perkin Elmer 100 Series Fourier Transform Infrared (FTIR) spectrometer. Powdered marble sample was finely ground in a mortar and then mixed with potassium bromide (KBr) powder (1/100 by weight). The powder mixture was put in a 13 mm diameter mould and pressed at high pressure using a hydraulic press to form thin pellets. In order to minimize the amount of water adsorbed, the pellets were heated in a furnace overnight at 100 ºC. Spectra data were recorded and analysed using the Spectrum 10™ software within the 4000 - 450 cm^{-1} spectral range in transmission mode.

Thermal analysis, i.e. thermogravimetry (TG) and differential thermal analysis (DTA), were performed by using a SETARAM LABSYS system, from ambient temperature to 1000 °C, using a 20 °C/min heating rate and a 100 ml/min nitrogen flow. The measurement was made using about 8 mg of powdered marble in a 100 μL alumina crucible.

3. Results and Discussion

3.1 Measurements of pH and carbonate content

The pH of the suspensions indicates the level of alkaline or acidic species contained in the marble powder. The average pH values of the IDA marble sample (Fig.3) are approximately equal to 8.5 for suspensions stirred for 24 h and 48 h. These measured pH values are therefore higher than the neutral pH value (7.00), showing that suspensions are basic: an indicator of the presence of alkaline species in the IDA marble powder. These results are close to those reported by Ahmed et al., [10] on the potential use of marble and granite solid wastes as environmentally friendly coarse particulate in civil construction.

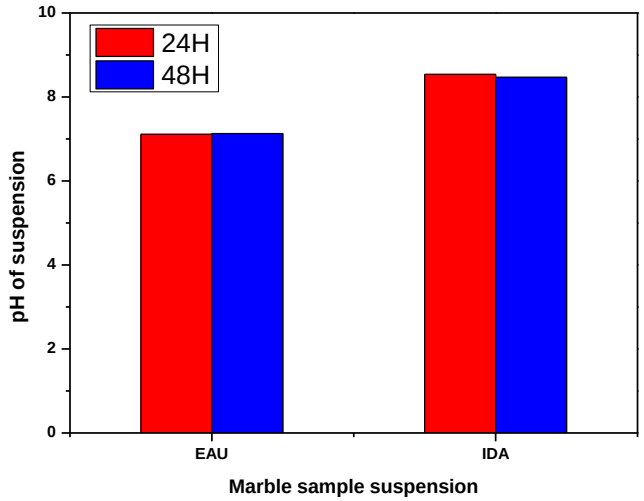

Figure 3: The average pH of the IDA marble sample

The percentage carbonate content in the IDA marble sample is presented in Fig 4. This result revealed high carbonate content (99.6 wt.%) for IDA sample. This suggests that IDA sample is carbonated.

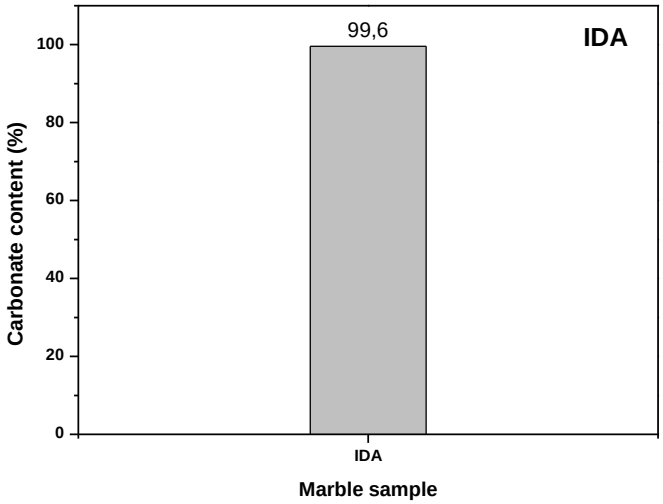

Figure 4: Carbonate content of the IDA marble sample

3.2 Particle Size Distribution

From the particle size distribution results presented in Fig. 5, the IDA sample could be categorized into three size fractions. The first size fraction is in the range of 250 μm and 500 μm, the second size fraction is between 125 μm and 250 μm; and the third size fraction is between 63 μm and 125 μm. These results showed that for the marble powder sample, only about 21 wt.% of the grains have a size < 63 µm and therefore, can be used to reinforce concrete.

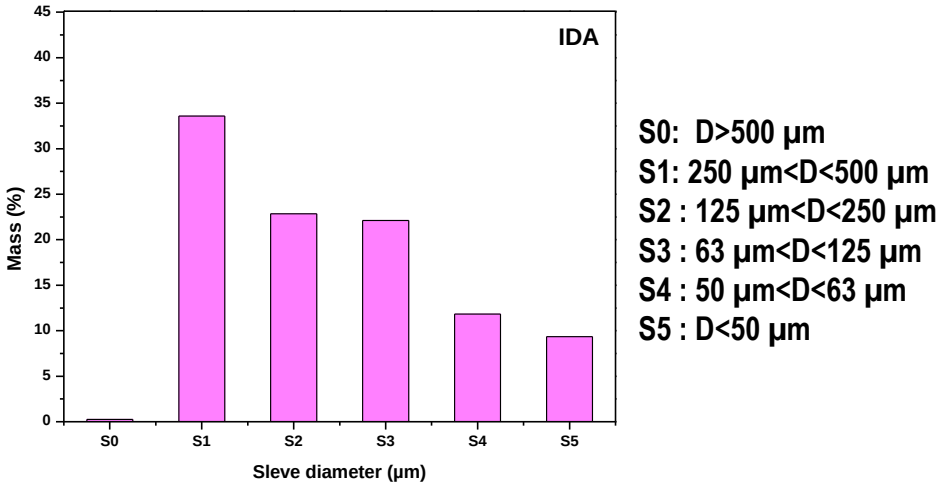

Figure 5: Histogram of the granulometric repartition of the IDA marble powder

3.3 X-ray Diffraction (p-XRD)

Fig. 6 shows the p-XRD pattern of the IDA marble sample. The diffraction peaks of IDA sample were matched with ICDD PDF-no. 01-085-1108 which indicated the presence of Calcite ($CaCO_3$). There are only peaks of calcite indicating IDA marble is a pure calcite. Attributions of calcite reflections are in good agreement with those reported on marbles characterization [4][8][34][35][36][37].

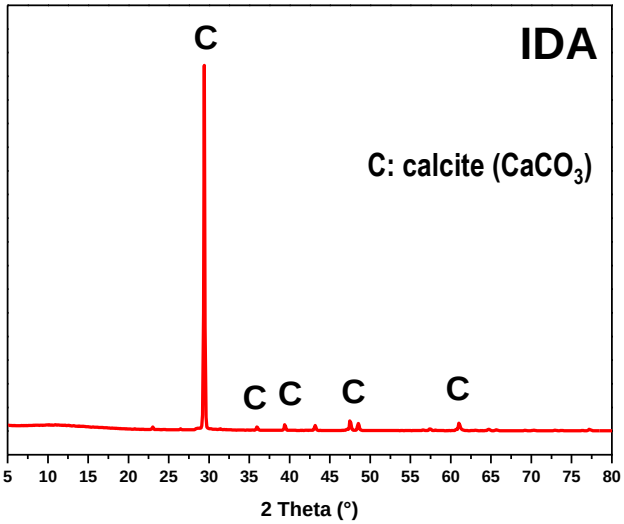

Figure 6: XRD pattern of IDA marble sample

3.4 XRF chemical analysis

The chemical composition of the IDA marble sample was determined by an X-ray fluorescence spectrometer. The analysis revealed the results grouped in Table 2 below.

Table 2: Chemical composition of the studied marble powder sample (% by weight).

Sample	**Composition in %**								
	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	LOI	TOTAL
IDA	55,91	00,36	00,00	00,11	00,02	00,00	00,00	43,30	99,70

According to Table 2, for the IDA sample, there is only calcium oxide (CaO) at a high content (55.91%) indicating mainly the presence of calcite ($CaCO_3$) [9][11] whose theoretical composition in CaO is 56%. The loss on ignition, symbolized by P.F., essentially represents carbon dioxide (CO_2) from the calcite contained in this sample and revealed by X-ray diffraction. The percentage of other oxides (MgO, SiO_2, Al_2O_3, K_2O, Na_2O and Fe_2O_3) in the IDA sample is insignificant or zero, indicating that the calcite of IDA is of high purity.

3.5 Fourier Transformed Infrared Spectroscopy

Fig. 7 shows the FT-IR analysis spectra of the IDA marble sample. The main bands of absorption obtained from Fig. 6, are regrouped in Table 3.

Table 3 Main bands of FT-IR absorption and associated bond vibration of IDA marble sample

Fundamental frequencies (cm^{-1})		**Modes of vibration**
713	ν_4	In-plane bending mode of CO_3^{2-}
877	ν_2	Out of plane bending mode of CO_3^{2-}
1414	ν_3	Asymmetric stretching mode of CO_3^{2-}
1810	$\nu_1 + \nu_4$	Combination of vibrations of ν_1 and ν_4
3470	ν	Symmetric OH stretch in H-O-H

The spectra of IDA marble sample shows the bands observed at 713 cm^{-1}, 877 cm^{-1}, the broad band at 1414 cm^{-1} and 1810 cm^{-1} representing vibration bands of carbonate radicals which is due to the presence of calcite mineral [38][39] in the IDA marble sample. This result corroborated with those obtained by carbonate content (section 3.1), XRD (section 3.3) and XRF (section 3.4) in this study, revealed the major presence of calcite in the IDA marble.

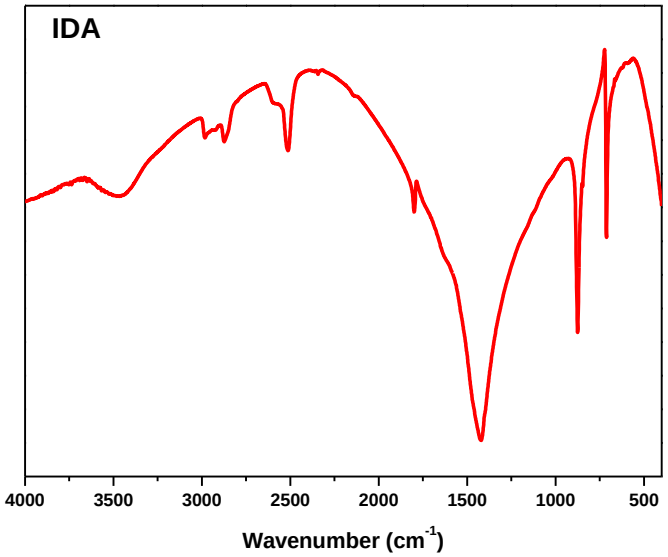

Figure 7: FT-IR spectra of IDA sample

3.6 Thermogravimetric/Differential Thermal Analyses

The TGA/DTA curves show the thermal decomposition under nitrogen flow for the IDA sample.

The curve of the IDA sample (in Fig. 8) shows a loss of mass. This mass loss begins slowly from 370°C to 625 °C (i.e. 2.9 %) and increases between 625 °C and 870 °C with a loss of 41.5 % i.e. a total loss of 44.4 %. This is due to the decomposition of calcium carbonate (calcite) into calcium oxide (CaO) and carbon dioxide (CO_2) according to equation (3). It is this decomposition that the ATD curve shows through the endothermic peak at 800°C. These thermal curves observed for the IDA marble sample in this study are similar to those reported in the literature on natural calcite marbles [8][40]. This decomposition reaction give the following equation:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (3)$$

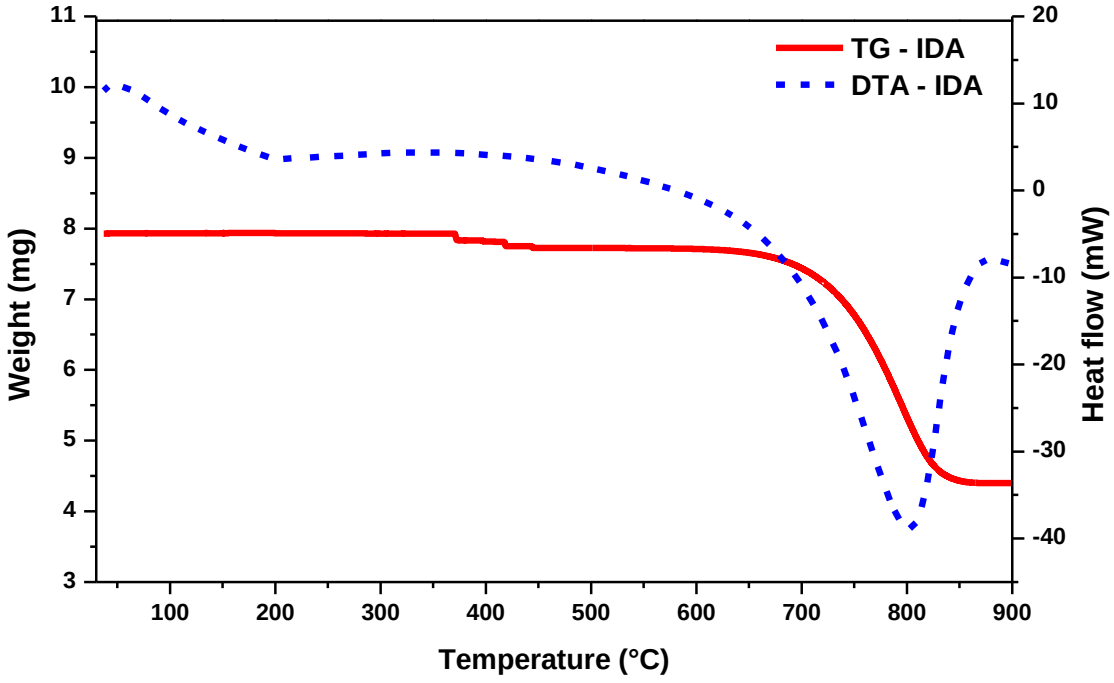

Figure 8: TG-DTA curves of IDA marble sample

4. Conclusion

The following conclusions have been drawn from this study: IDA marble sample is pure calcite. This sample is very white and basic (pH ≈ 8.5). The particle size study of the powder of this sample shows two major size fractions: 23 % of the particles have a size between 125 µm and 250 µm and 34 % of the particles have a size between 250 µm and 500 µm.

In view of the physico-chemical characteristics determined for the IDA marble sample, different uses can be envisaged. IDA sample is calcite and therefore can be used in various industries such as the production of paper, paint, fertilizer, cement, mortar and concrete, functional construction materials, and pharmaceutical industries. IDA marble can be used as a precursor for the production of apatite, gypsum and its derivatives like plaster and chalk.

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