Geochemical Characterization of Carbonate Rocks of the Uíge's Municipality (Angola), for Cement Industry

Carla Marina Nicolau Tunguno(✉), Gomes Guenge Mucanza, and Pedro Claude Nsungani

Universidade Agostinho Neto, Avenida 4 de Fevereiro, nº 71, Luanda, Angola
carlatunguno2012@gmail.com, gomes.mucanza@gmail.com, pedroclaudensugani@yahoo.com.br

Abstract. The Carbonate rocks from Angola were studied from a geological perspective and as mineral resources. However, the petrological and geochemical characteristics need to be analyzed and studied in order to evaluate their industrial qualities. The general purpose of this work is to analyze the geochemical suitability of the carbonate rocks in Uíge's Municipality (Uíge province) to be used in the cement industry. To achieve this purpose, a methodology based on field survey and sampling was applied and laboratory tests were performed, namely petrographic and geochemical analyses. The results obtained showed that the carbonate rocks of the Uíge's Municipality, are suitable for the cement industry, especially for the Portland and White cement.

Keywords: Geochemistry · Carbonate rocks · Cement industry · Uíge's municipality and Angola

1 Introduction

The carbonate rocks from Angola were studied from a geological perspective and while mineral resources [1].

Since the country is in the process of national reconstruction, there is a significant demand for this raw material for the development of the different industries currently being implemented, such as cement, paper, white ceramics, chemical, glass, paint, metallurgy, steel, soil Ph correction, etc., in which one of the raw materials used is carbonated rocks.

At present, and in view of the construction and reconstruction program of the Uíge's Municipality, there is a great demand for natural resources, namely carbonate rocks (Limestone).

In this sense the general purpose of this work is to analyze the geochemical suitability of the carbonate rocks of the Uíge's Municipality to be used in the cement industry.

A. G. Correia et al. (Eds.): ICITG 2019, SSGG, pp. 114–121, 2020.
https://doi.org/10.1007/978-3-030-32029-4_10

2 Materials and Methods

The methodology used consist of the following steps:

a. Field survey: The methodology applied for the accomplishment of this work comprised the survey of field and sampling where the topographic map was used at scale of 1/250,000 edition 1990 - Sheet nº 17 [2] and the geological map of Angola at scale of 1/250,000 sheet South B-33/V (Carmona - Sanza Pombo) [3], respectively. During this stage 12 outcrops were studied and 31 samples were collected.
b. Petrographic Analysis: The petrographic analyzes were carried out at the Macroscopy and Microscopy Laboratory of the Sciences Faculty of Luanda, Agostinho Neto University. Color, texture and mineralogical composition of the selected samples were performed by unaided eye. Thin sections were prepared in order to determine the cement, porosity, recrystallization and other diagenetic aspects.
c. Calcimetry analysis: These analyzes were made at the National Laboratory of Engineering of Angola (LEA), and consisted of the following tasks:
   - Crushing: crusher jaws in granules <2 mm and uniform dismantling of 20 to 30 g each;
   - Sieving: used the 100 μm sieve, Mesh nº 300;
   - Weighing and acid attack: 4 g of powdered sample was used with HCL (3 to 5 ml);
   - Filtration and drying: elimination of HCL with addition of distilled water and dried in the oven at 130° C for 120 mm;
   - Weighing and analysis of the residue: to verify the existing mineralogy.
d. Geochemical Analysis: On the samples mentioned above, the geochemical analyzes were done at the GeoBiotec Laboratory of the University of Aveiro, Portugal.
   - Dissolution of the carbonate rocks: for the determination of the main content of the carbonate rocks;
   - Analysis of major, minor and trace elements. X-ray fluorescence spectrometry (XRF);
   - Characterization of the rock type and its designation.

3 Results

The petrographic characterization of the carbonate rocks from this municipality were carried out essentially by the study of outcrops in seven (7) neighborhoods: Tomessa, Aldeia Macalé, Quimango, Mbaza Polo, Henda, Kimassu and Kixikongo, where thirty one (31) samples were collected, but only twenty two (22) were analyzed.

The designation of the samples was based on two criteria: classification of Folk [4] taking into account the percentage of allochemicals present and the matrix, and classification of Dunham [5], according to the depositional texture of the carbonate rocks.

For better understanding, some samples will be described, and the other results listed in the Table 1.

Sample HEDA. In this case, calcite, quartz and some quartz inclusions were observed microscopically (Fig. 1). The packing is closed and the texture is supported by sparite block. Being a grain-supported, denominated like Compact Limestone (lime-packstone).

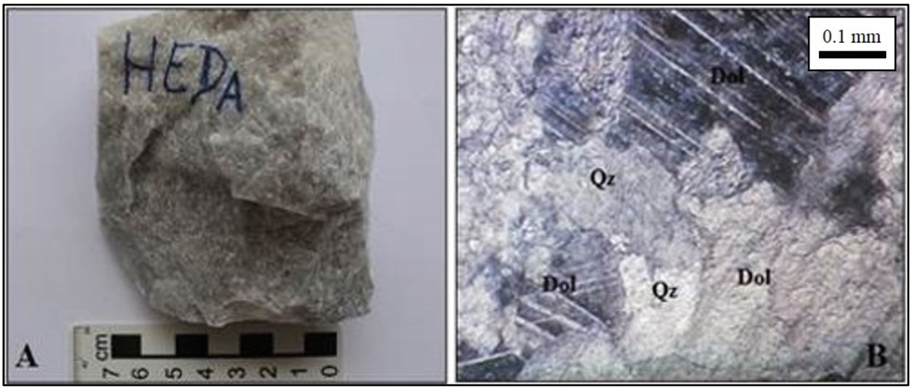

Fig. 1. Sample HEDA: (A) Macroscopic and (B) Microscopic.

Sample PC6. Mineralogically, its consists of considerable amount of quartz, a slight percentage of calcite, muscovite and some mafic minerals (Fig. 2). This sample shows some laminations. According to [6], this sample is considered Calcarenite.

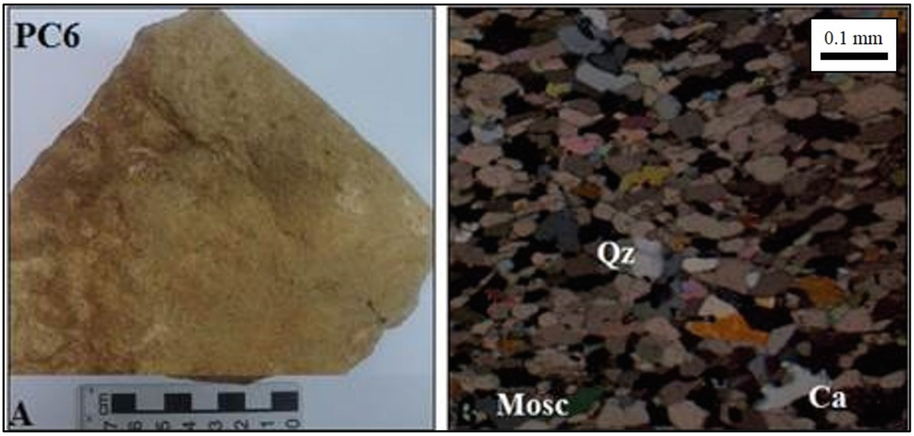

Fig. 2. Sample PC6: (A) Macroscopic and (B) Microscopic.

Sample TOM1. This sample consists of calcite, dolomite, quartz and white mica (muscovite) (Fig. 3). Microscopically it consists of medium to coarse grains with moderate selection. It was denominated Compact Limestone.

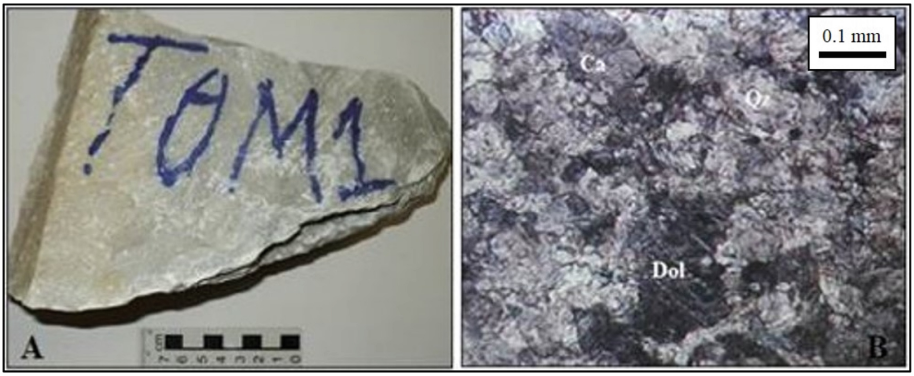

Fig. 3. Sample TOM1: (A) Macroscopic and (B) Microscopic.

The macroscopic description of the samples, the examination of the texture and the composition in thin section allowed to establish five (5) types of most important lithotypes, listed in Table 1.

Table 1. Results of petrographic analyzes.

Sample	Lithotypes	Sample	Lithotypes
TOM2	Crystalline limestone	PC6	Calcarenite
MUC2	Granular limestone	HEDA	Compact limestone
TOM1	Compact limestone	TOM3	Oolitic limestone
QUIM1	Granular limestone	MUC1	Dolomite
PV3A	Compact limestone	PIK1	Limestone oobiosparite
PV3B	Granular limestone	PC2	Crystalline limestone
HEDB	Wackestone	NZA1	Calcário Grainstone
MBP1	Granular limestone	NZA2	Oolitic limestone
MBP2	Granular limestone	NZA3	Oolitic limestone
PIK3	Calcarenite	PC2	Crystalline limestone
PIK6	Crystalline limestone	TOM 3	Oolitic limestone

As previously mentioned, 31 samples were collected, but only 22 have been submitted to the geochemical analysis, the results of which will be presented in Table 2.

With the CaO results representing calcium carbonate (limestone), MgO indicating the field of Magnesian carbonate rocks (dolomitic limestones), and FeOT indicating the field of marmoreal carbonate rocks, a diagram of lithofacies [7] (Fig. 4), where it was verified that all samples belong to the field of calcium carbonate.

In the study of the minor elements the Rb in the carbonated rocks is associated with clays. Rb occurs naturally in the form of oxides, associated with alkali metals such as potassium (K) and sodium (Na) [8]. The results of the samples from the Uige's Municipality show that the Rb contents range from 0.7 - 109 ppm.

Table 2. Results of the geochemistry of the larger elements.

Sample	CaO (%)	MgO (%)	SiO2 (%)	Al2O3 (%)	FeO (%)	Fe2O3 (%)	Na2O (%)	P2O5 (%)	TiO2 (%)	K2O (%)	MnO (%)	SO3 (%)	Cl (%)	F (%)
HEDa	54.52	0.86	1.02	0.39	nd	0.12	0.02	0.05	nd	0.03	nd	nd	nd	nd
HEDb	54.52	0.53	0.51	0.24	nd	0.09	0.02	0.06	nd	0.03	nd	0.16	nd	nd
HEDc	54.34	0.44	1.37	0.17	0.08	nd	0	0.03	**0.01**	0.06	0	0.06	0.06	0
MBP1	55.07	0.5	0.79	0.36	nd	0.13	**0.01**	0.08	nd	0.05	nd	nd	nd	nd
MBP2	55.56	0.38	0.44	0.2	nd	0.08	nd	0.05	nd	0.02	nd	0.03	nd	nd
MUC1	48.59	0.82	7.74	1.71	**0.67**	0	0.03	0.05	**0.11**	0.16	0.04	0.13	0	**14.73**
MUC2	46.7	7.79	**0.24**	**0.05**	nd	**0.03**	nd	0.04	nd	**0.01**	nd	0.05	nd	nd
NZA1	51.05	1.17	4.09	0.73	0.44	0	0	0.04	0.05	0.18	0.01	**0.76**	0.04	0
NZA2	52.9	1.04	2.52	0.27	0.16	0	0	0.04	0.01	0.06	0	**0.01**	**0.16**	0
NZA3	50.5	0.84	5.4	1.12	0.43	0	0.02	0.07	0.04	0.23	0.01	0.74	0.07	0
PC2	28.51	19.93	7.25	0.18	0.16	0	0	**0.02**	0.02	0.02	0.03	0.18	0.05	0
PC6	**25.38**	14.39	17.72	**1.94**	0	**0.91**	0.23	**0.11**	0.1	**1.01**	**0.06**	0	0	0
PIK1	31.47	21.62	0.28	0	**0.02**	0	**31.47**	0	0	0	0.02	0	0.05	0
PIK3	30.63	**25.54**	**22.86**	0.32	0	0.15	0.02	0.11	0.02	0	0	0.06	**0.01**	0.63
PIK6	**58.92**	1.25	2	0	0	0.19	0.09	0.03	0.02	0.05	0	0	0	0
PV3A	55.04	0.49	1.83	0.34	nd	0.13	nd	0.05	nd	0.06	nd	0.14	nd	nd
PV3B	55.59	0.69	1.14	0.3	nd	0.15	0.04	0.04	nd	0.05	nd	0.07	nd	nd
QIM1	53.31	1.03	1.55	0.5	nd	0.17	0.01	0.05	nd	0.08	nd	0.01	nd	nd
TOM1	55.11	**0.34**	0.34	nd	nd	0.1	0.03	0.06	nd	0.04	nd	nd	nd	**0.37**
TOM2	55.44	0.41	1.01	0.27	nd	0.17	0.08	0.04	nd	0.02	nd	0.02	nd	nd
TOM3	53.08	1.13	1.55	0.15	0.09	nd	0	0.06	0.01	0.02	**0.01**	0.17	0.05	0

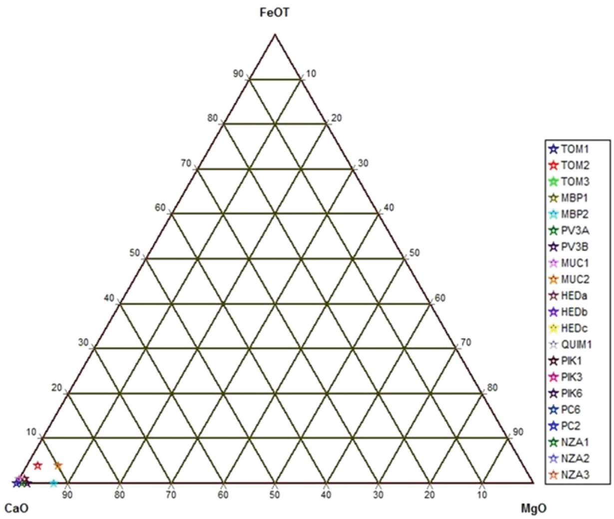

Fig. 4. Diagram of litofaces of carbonate rocks of Uíge.

Mn (22.1–137.3 ppm), Sr (36.5–6389.8 ppm) and Ba (5.1–320 ppm) (Fig. 5) elements that may be present in the chemical composition of carbonate minerals.

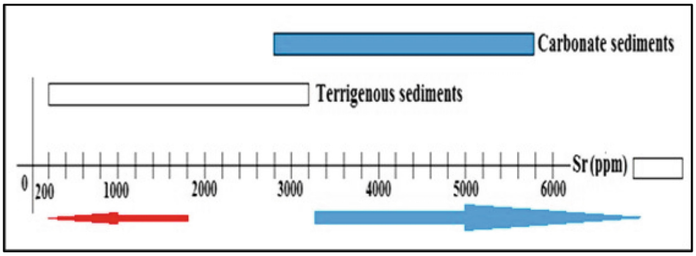

Fig. 5. Graph of the sediments with respect to Sr [9].

The Sr contents of the samples range from 36.5–6389.8 ppm. Based on these values, most of the samples correspond to carbonate sediments (Fig. 6), which indicates that they belong to the Back-bulge depozone [10–12].

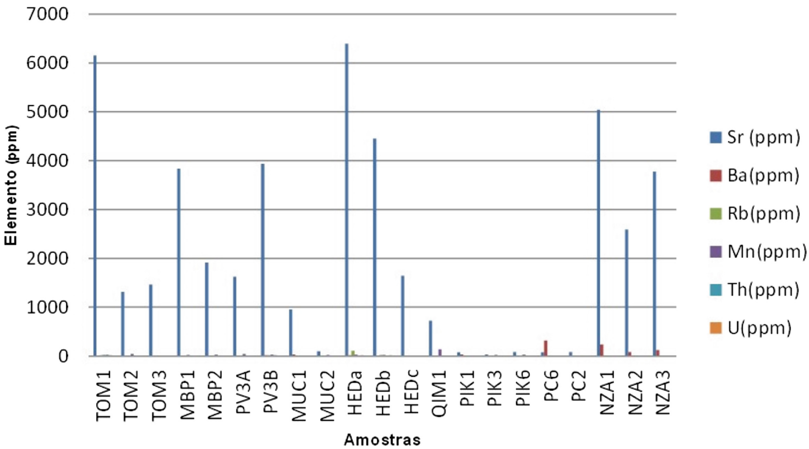

Fig. 6. Distribution of minor elements in samples from the Uíge municipality.

4 Discussion

Geologically the studied carbonate rocks were formed in a basin of the compressive type or foreland, in an underwater system, with the possible occurrence of clay materials and important sedimentation of shallow marine water, with the formation of carbonaceous ramps of small thickness of sediments.

The carbonate rocks of the area of the Uíge's municipality show an alternation of metric layers with indications of metamorphism of low degree well evidenced in the thin blades.

The chemical analyzes of the largest elements of the samples of the studied area allow to locate the limestones as belonging to the Alto-Chiloango Subgroup (Proterozoic medium) of the finely laminated calcareous type.

Samples from the Uíge's Municipality are rich in calcium, but poor in magnesium, iron and phosphorus, varying the concentration of silica. Which indicates a more calcium composition.

According to the analytical data and compared with the national [13] and international standards [14, 15], it was verified that the majority of the samples of the area studied are adequate for the manufacture of Portland cement.

The main raw material of the cement, lime (CaO) from $CaCO_3$, presents a high content (Table 3) in the samples collected within the study area.

Table 3. Chemical concentrations and modules in the Uíge municipality.

Chemical Parameters	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O
Average %	48,8	3,9	0,44	0,12	4,82	0,12	0,1	1,5
Modules or factors	Formulas				Standard for fabrication of common cement			
					Accept		Obtained	
Silica factor	% SiO_2/(% Al_2O_3 + % Fe_2O_3)				2 a 3,5		7	
Alumina factor	% Al_2O_3/% Fe_2O_3				$\geq$0,66		3,8	
Lime saturation factor	% CaO * 0,7 (% SO_3)/(2,8% SiO_2 + 1,2% Al_2O_3 + 0,65% Fe_2O_3)				0,66 a 1,02		4,4	
Plaster factor	1,7 (% SO_3)				–		–	

The samples that are adequate to this industry are: HEDa, HEDb, MBP1, MBP2, PIK6, PV3a, PV3b, QUIM1 and TOM1. This behavior is different for samples PIK1, PC2 and PC6, meaning they have low CaO content (25.38 and 30.63%) and high MgO, SiO_2 and Al_2O_3 contents.

Thus, according to Table 3, it was verified that the calculation of the Siliceous Module (MS) in the Uíge's municipality is 7, and that is above the established norms. The result of the aluminous module (MA) is equal to 3.8%, which is within the established limits which make easy the rapid combination of the oxides at high temperatures. The lime saturation factor (LSF), equal to 4.4%, is above the limits established by the standards, which makes clinker easier to grind.

5 Conclusions

After completion of the work, the following is concluded:

The limestones in the Uíge municipality can be used as raw material for both Portland and White cement, provided that special treatments (processing) with addition of other materials are made to increase the content of SiO_2 and Fe_2O_3. The other applicable treatment is reducing the content of clays by dry or wet sieving process (mechanical process consisting of the separation of the coarse and fine particles).

6 Recommendations

Based on the results obtained the following is recommended:

- Elaboration of a more detailed project to determine the reserve potential of the area;
- To carry out further study of the carbonate rocks in this area, since this is the first work that was performed under this subject.

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