

# Physicochemical Characterisation for Potential Uses as Industrial Mineral of Bauxite from Débélé, Guinea

# Mamadou Yaya Balde<sup>1,2</sup>, Chantale Njiomou Djangang<sup>1\*</sup>, Ramatoulaye Binta Diallo<sup>2</sup>, Philippe Blanchart<sup>3</sup>, Daniel Njopwouo<sup>1</sup>

<sup>1</sup>Department of Inorganic Chemistry, University of Yaounde I, Yaounde, Cameroon <sup>2</sup>Department of Chemistry, University Gamal Abdel Nasser of Conakry, Conakry, Guinea <sup>3</sup>Institute of Research for Ceramics—IRCER, Limoges, France Email: \*djangangc@yahoo.fr

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## Abstract

Assessing the potential uses as industrial mineral, bauxite from Débélé, Guinea, has been characterised by chemical and mineralogical analyses, the determination of the amorphous content, the rate of portlandite consumption in an aqueous solution, the strength activity index, and the thermal behaviour up to 1200°C. It was evidenced that the raw sample is gibbsite-rich type bauxite with about 45.06 wt% of alumina, 23.80 wt% of iron oxide, and 1.74 wt% of silica. It meets the chemical composition required for bauxites used for refractory cement. During heating, the raw bauxite undergoes high densification with low linear shrinkage, motivating a potential use in dense ceramic compositions with high thermal stability. Also, the heating at only 600°C gives a significant pozzolanic activity in combination with Portland cement. The correlation between the pozzolanicity, the amorphous phase content, and the specific surface area indicated that the raw and the calcined materials present an interesting reactivity for using them in alternative cement formulations.

## **Keywords**

Bauxite, Characteristics, Industrial Mineral, Guinea

# **1. Introduction**

Bauxite is a source of diverse aluminum ores, with a high content of hydrated aluminum oxides such as gibbsite, boehmite, and diaspore. Apart from the metallurgical usage, bauxite has found diverse applications in manufacturing various products like cement, abrasives, refractories, chemicals, etc. Recently, bauxite has been used as an additive in various material compositions, to improve functional properties or for alternative sustainable products [1]-[6]. The industrial use of bauxite and derivatives materials is mostly based on the high aluminum hydroxide content, as gibbsite or boehmite. Gibbsite is mostly found in the clayed fraction of bauxite, as a secondary phase. It has many valuable effects on ceramic and cement applications due to the unique properties provided by alumina. As cementitious additives, gibbsite reacts with portlandite, having beneficial effects on cement hydration and paste rheology [4] [5] [7] [8] [9]. It was found that the replacement of Portland cement by gibbsite up to 12.5 wt% contributes to the significant reduction of the setting time of pastes, the two times increase of the mechanical strength, and the reduction of porosity. They are related to the high amount of ettringite crystals in the matrix that is favoured by the presence of gibbsite [5]. Besides, bauxite and bauxite derivatives have been used in valuable refractory ceramics, ceramic, and glass products. It is from the unique properties induced by the different forms of alumina obtained during the thermal process. They decrease the fluxing role of alkaline minerals, favouring the high mechanical resistance of products [10] [11] [12] [13] [14]. Beyond, bauxite found further application in water treatment, satisfactory elimination of certain toxic elements such as fluorides was obtained thanks to the improvement of adsorbent properties through the chemical and heat activation [6].

Recalling the sustainable approaches in different technological processes, they are also from the very large availability of raw material, and the related socio-economic development from local resources valorization. Guinean bauxite deposits are one of the world's main reserves that are used for metallurgical purposes by foreign companies [15] [16] [17] [18] [19]. The broader exploitation of this largely available resource is fundamental for socio-economic development, especially in the context of a developing country. The impact can be more effective if they are used in manufacturing building materials, electronics, and medical devices, or many more industrial and domestic products. This would enhance the development of local industries, with subsequent benefits like the creation of job opportunities, reduction in the cost of materials, and value-added welfares. The large scale of possible applications of this mineral resource is mostly based on the specific physicochemical characteristics. However, they are changing from one geographical site to another. It is essential to perform studies in potential uses according to the provenance. The present work aims to initiate investigations on bauxite quarried in Débélé site, Guinea, focusing on the chemical and structural compositions as well as on the thermal behaviour and the pozzolanic activity. It is a valuable contribution to the scientific database that can stimulate further development works.

## 2. Methods

#### 2.1. Studied Material Area

The sample of bauxite used was quarried from the large deposit of Débélé lo-

cated in Kindia Region of Guinea. It is the south-western part of the Bove Basin at 9°53'N - 13°07 W (**Figure 1**). In comparison to previous geochemistry investigations carried out in this area, the sample is similar to a lateritic type that is formed in situ. It belongs to one of the two main types of bauxite that are associated with a sedimentary type founded in this area. The former type is characterised by its lower amount of alumina (30 - 60 wt%) in comparison to that of other types (60 - 80 wt%) [18] [19].

#### 2.2. Material Sampling and Characterisation

The as-received samples were dried at room temperature, crushed, and sieved below 75 µm, to obtain a powder with a red colour; 2.5YR4/8 according to the Munsel code [20]. The true density of the powder was measured with a helium pycnometer (micrometric model ACCUPYC 1330). The amorphous phase (*AP*) content was measured by vigorously stirring a mixture of 2 g of powder ( $m_i$ ) with 30 ml of an 8 M sodium hydroxide. The subsequent addition of 30 ml of 0.5 M hydrochloric acid solution at 50°C for 5 minutes is followed by washing with distilled water and centrifugation, to obtain a neutral pH residue that was dried at 110°C until a constant mass ( $m_i$ ). The amorphous content is given by Equation (1) [12].

$$AP(\%) = \frac{m_i - m_f}{m_f} \times 100 \tag{1}$$

The specific surface area (SSA) of the cement powder was measured by N<sub>2</sub> adsorption in BET [21]. The chemical composition was obtained by X-ray fluorescence spectrometry (XRF) using a Bruker S8 apparatus and the mineralogical composition was obtained by X-ray powder diffraction (XRD) with the grounded sample below 40 µm, using a Bruker D8 Advance diffractometer (copper anode:  $\lambda = 1.5418$  Å; graphite monochromator; step size of 0.01° 2 $\theta$ , 0.1 s per step). Crystalline phases were identified by comparing the models with the standards of the powder diffraction files. This analysis was completed by infrared spectroscopy (FTIR) using a Bruker spectrometer in the absorbance mode between wavenumbers of 4000 and 400 cm<sup>-1</sup>. Samples were obtained by the KBr cap method. Thermal analyses, DTA (Differential thermal analysis) and TGA (Thermogravimetric analysis) were performed with a TA instrument Q600 SDT under a flow rate of dry air (100 ml/min). The semi-quantitative mineralogical compositions of samples were calculated using the method developed by Njopwouo (1984) and Yvon et al. (1990) [22] [23]. Calculated data were correlated with thermal and chemical results, and with XRD analyses. The sintering behaviour was characterized up to 1200°C with a DI 24 ADAMEL dilatometer with a heating rate of 5°C/min.

The pozzolanicity degree was obtained considering the consumption of calcium hydroxide (CH) in an aqueous solution, by the Modified Chapelle Method [9]. The determination of the amorphous phase quantity and the Modified Chapelle Method was carried out simultaneously with both the raw sample and the



Figure 1. Study area location: (a) Guinea's location in the world; (b) Kindia and Conakry with Maritime Guinea and its location in Guinea; (c) Geological map of the study area showing Balaya plateaus and its surrounding area and (d) Sampling location in the local geology [18] [19].

calcined product at 600°C, inside a muffle furnace (heating rate of 5°C/min). To complain about the ASTM C618 standard, the chemical composition was considered in results since the limiting value of mass percentages of  $Al_2O_3 + SiO_2 + Fe_2O_3$  must be 70 wt% for pozzolanic material. The strength activity index (I), which is also the quantification of pozzolanicity, was measured according to ASTM C109 and C618-94 [24] [25]. Specific, mortars were obtained by mixing 1/3 of the binder with 2/3 of the sand and with water, as indicated in the EN F 196-1 Standard [26].

Mechanical characterisations were obtained with cubic test samples ( $4 \times 4 \times 4$  cm). They were shaped from fresh mortars that were poured into metallic moulds. The compaction was improved by vibrations during 10 min (electrical vibrating table; M & O. type 202, N° 106) to remove entrapped air bubbles. The setting was under plastic films in a controlled air atmosphere (HR 100%; 20°C). After 28 days of setting, the compressive strengths (*Rc*) of test samples were measured by NF P18-406 [27], using a hydraulic press (LMC type C004, No. 89/54800). The peak strength values were obtained considering a polynomial correction method that is:

$$F(\text{in KN}) = 1.02 \times X \pm 0.24$$

where *X* is the read value (KN).

The compressive strength *Rc* (MPa) is given by Equation (2):

$$Rc = \frac{F}{S} \tag{2}$$

where *F* is the breaking strength (N) and *S* is the cross-section of the specimen in mm<sup>2</sup>.

The strength activity index (*I*) was calculated using Equation (3):

$$I = 100 \times \frac{Rc_{28j} \left(HM\right)}{Rc_{28j} \left(CM\right)}$$
(3)

where  $Rc_{28j}(HM)$  is the compressive strength after setting of a hybrid mortar where 20%wt% of Portland cement is replaced by the bauxite powder.  $Rc_{28j}(CM)$ is the compressive strength of the reference mortar containing 100% of Portland Cement.

# 3. Results and Discussion

#### **3.1. Physical Characteristics**

From **Table 1** presenting some physical parameters of the bauxite sample, the absolute density of the powder is 2.66 g·cm<sup>-3</sup>, which is slightly higher than that of gibbsite (2.42 g·cm<sup>-3</sup>). This value outlines the high degree of compaction at the crude state since it is an important intrinsic parameter of the material at the specific granulometry. It is therefore useful for monitoring and understanding the performance when shaping products based on the studied material [28].

The amount of amorphous phase in the raw bauxite is 30.8%, and it raises 51.2% after calcination at 600°C. The significant increase of amorphous phase content with heating is related to a reactivity improvement since phases react easily with others in mixtures due to higher free energy in comparison to that of the crystallised phases. The amorphous content is therefore a leading factor for the use of a material as a mineral additive in the cementitious matrix or for the formulation of alternative cements such as geopolymers [29] [30]. As for the pozzolanic degree, the bauxite powder sample exhibit a value of 748 mg of CH fixed per gram of sample, which is close to the lower limiting value of 700 mg reported in the ASTM C618-94 standard for pozzolanic material. Correspondingly, the calcined sample (CB) presents a very high value of 999.9 mg of CH fixed per gram of sample. The same trend can be observed with the mechanical activity index which is 71%, and this value is similar to that from most of the cementitious materials reported in the literature [9] [31] [32].

Table 1. Physicochemical characteristics.

Parameters	Raw (RB)	Calcined (CB)
Absolute density (g·cm <sup>-3</sup> )	2.66	-
Specific surface area: SSA $(m^2 \cdot g^{-1})$	3.60	4.32
Amorphous phase (%)	30.8	51.2
Mass of CH* (mg) fixed	748	999.9
Activity index: I (%)	71	72.7

\* CH is from the Modified Chapelle Method.

### 3.2. Chemical Composition and Structural Characteristics

The chemical composition of the studied sample (Table 2) showed the predominance of alumina  $Al_2O_3$  (46.06 wt%), the presence of iron oxide  $Fe_2O_3$  (23.80 wt%), and small amounts of silica SiO<sub>2</sub> (1.74 wt%) and titanium oxide TiO<sub>2</sub> (1.74 wt%)wt%). The loss of ignition is 25.60 wt%. It is a typical composition of lateritic bauxite, as it was reported by published studies about that geographical area [20] [21] [33]. This composition is similar to that of bauxites used for refractory cement since the compositional range is 45 to 60 wt% of alumina; up to 25 wt% of iron oxide; below 5 wt% of silica [34]. From the XRD pattern (Figure 2), gibbsite was identified as the major phase, the other minerals are hematite, quartz, and anatase. Gibbsite is then the only mineral containing aluminum oxide, accordingly, from the proportion of the latter obtained by XRF, that of gibbsite was evaluated to 70.5 wt%. Also, the DTA and TG analyses in Figure 3 show a large endothermic peak and a weight loss at 311°C. It is related to the partial dehydroxylation of gibbsite giving boehmite (Equation (4)). At 380°C, an embedded small peak is also ascribed to gibbsite transformation into boehmite that often occurs in the range of 300°C - 310°C. However, the temperature range can be shifted to 350°C - 380°C with well-crystallised gibbsite. The phase transformation is written in Equation (4):

Table 2. Chemical and mineralogical composition of the studied bauxite.

Chemical composition			
$Al_2O_3$	46.06		
Fe <sub>2</sub> O <sub>3</sub>	23.80		
SiO <sub>2</sub>	1.74		
TiO <sub>2</sub>	1.74		
CaO	0.06		
$P_2O_5$	0.06		
Cr <sub>2</sub> O <sub>3</sub>	0.18		
SO <sub>3</sub>	0.09		
MgO	<0.01		
Na <sub>2</sub> O	<0.01		
K <sub>2</sub> O	<0.01		
LOI	25.6		
Total	99.36		
Mineralogical composition			
Gibbsite	69.50		
Hematite	23.80		
Quartz	1.74		
Anatase	1.74		
Total	96.78		



Figure 2. Diffractogram of the bauxite sample.



Figure 3. DTA/TGA curve of the bauxite sample.

$$Al(OH)_2 \rightarrow AlO(OH) + H_2O$$
 (4)

At higher temperatures, a less pronounced endothermic peak is at 520°C. It corresponds to the conversion of boehmite into  $\gamma$ -alumina (Equation (5)) [35] [36] [37] [38]:

$$2\text{AlO}(\text{OH}) \rightarrow \gamma - \text{Al}_2\text{O}_3 + \text{H}_2\text{O}$$
(5)

The total weight loss for the whole process is 24 wt%, and since gibbsite is the only mineral that undergoes mass loss as state above in relation to the departure of OH groups, the total gibbsite content is calculated to 69.5 wt%. Finally, a semi-quantitative composition can be obtained from information provided by the chemical, thermal, and XRD analyses. It gives 69.50 wt% of gibbsite, 23.80 wt% of hematite, 1.74 wt% of quartz, and 1.74 wt% of anatase. Gibbsite quantity obtained (70.5%) from XRF data (**Table 2**) is very close to that obtained from the TGA curve (**Figure 3**) 69.5%, with a deviation of 1%, reflecting very good correlation between the two methods. This compositional range indicates that the studied bauxite is a class 2 bauxite containing less than 80 wt% of gibbsite and more than 20 wt% hematite [1] [3].

Observations on the structural characteristics of the studied bauxite agree with

FTIR analyses presented in **Figure 4**. The behaviour of the raw bauxite is compared to that of the heat-treated material at 600°C. In **Figure 4** the raw bauxite exhibited absorption bands grouped in three regions: at 3619, 3525, 3445, 3375 cm<sup>-1</sup>; at 1020 and 960 cm<sup>-1</sup>; at 800, 750, and 550 cm<sup>-1</sup>, they are all related to the stretching of hydroxyl groups (Al-OH) in gibbsite [1] [33] [39] [40]. The heat-treated sample (**Figure 4**) evidence that these bands have disappeared with the thermal treatment since the OH groups are not more after the departure of structural water. The remaining absorption bands are at 500, 470, and 447 cm<sup>-1</sup> for Si-O and Si-O-Si of quartz as well as for Fe-O of hematite.



Figure 4. Infrared Spectrum of RB: raw bauxite and CB: calcined bauxite.

#### 3.3. Sintering Behavior

The densification with a temperature of the bauxite sample, up to 1200°C as well as the densification rates plotted against time and temperature are presented in **Figure 5** and **Figure 6**.



Figure 5. Dilatometric curve of the bauxite sample.



Figure 6. Densification curve of the bauxite sample.

From the ambient temperature, there is a progressive dilatation up to 470°C, which is probably related to the activation of the system with heating. A consecutive shrinkage begins at 430°C, about the dehydroxylation of the gibbsite, which is accompanied by a peak of the densification rate at 530°C. A small variation of the dilatation is at 573°C, corresponding to the volume expansion of quartz grains during the polymorphic transformation of quartz  $\alpha \rightarrow \beta$ ; it is a reversible phenomenon since during cooling a volume reduction is seen at the same temperature. From 600°C to 977°C, densification occurs and becomes more accentuated (volume reduction of about 1vol %) below 977°C. It is related to the departure of structural hydroxyl in boehmite with the formation of gamma-alumina (y-Al<sub>2</sub>O<sub>3</sub>). Above 1000°C, the accentuated shrinkage is correlated with a peak at 1190°C in the thermal expansion rate curve. It is more likely related to the progressive transformation of aluminum hydroxide into transitional alumina phases, as  $\gamma$  or  $\kappa$  alumina, and finely  $\alpha$  alumina, increasing the crystallinity degree of phases [3] [40] [41]. The overall thermal transformation of the bauxite sample at 1200°C, lead to a total linear shrinkage of 3.2%. This relatively low value indicates that the studied bauxite is suitable in manufacturing dense ceramics, for specific applications requiring dimensional stability [12] [42].

#### 3.4. Discussion

The investigations on the physicochemical characteristics of the bauxite sample from Débélé evidence that the material is mostly composed of gibbsite. It is a well-known crystallized aluminum hydroxide mineral that is used in different industrials sectors and mostly in the manufacture of refractory materials. It is preferable to the other hydrated aluminum oxides because it readily dissolves to available alumina at low temperatures and pressures [41] [43]. In general bauxite exhibits interesting thermal behaviour and low firing shrinkage, which does not exceed 3.2% at 1200°C for the studied sample. Consequently, bauxite can be used for manufacturing dense ceramics having enhanced dimensional stability [42]. Besides, some of the properties of the studied sample are supposed to be beneficial in different sectors as for cementitious and geopolymer additives. When bauxite is heat-treated at 600°C some of the properties are significantly improved. It is evidenced in **Figure 7**, presenting the effect of temperature on different properties: the variation of the amorphous phase content (AP). The amount of the amorphous phase increases from 30.8% for the crude sample to 51.2% for the calcined sample at 600°C; the strength activity index (I) and the capacity to fix portlandite (m(CH)); the increase of the specific surface SSA.

The amorphous phase is the most active in the pozzolanic activity, and its quantity is a key characteristic of the material together with the specific surface area and the chemical composition. This promoting role is controlled by the relatively high free energy that exceeds that of the crystalline phase. Amorphous species are chemically more reactive with the surrounding particles. The increase of the content of the amount of amorphous phase is well correlated with the pozzolanic activity since it is the ability to fix portlandite in the presence of water ASTM C125-07 [44]. Reactivity processes are also related to the increase of SSA. From **Figure 7**, it increases with the calcination temperature from 3.60 to  $4.32 \text{ m}^2 \text{ g}^{-1}$ .

The interaction of portlandite with alumina is expected to be the dominant chemical reaction that is followed by the interaction of different oxides. They are mostly silica and iron oxide, considering the chemical composition of the studied bauxite (**Table 2**). Correspondingly, the mass of CH fixed per gram of sample has increased with the temperature, from the limiting value of 748 mg to a higher value of 999.9 mg. It is significantly higher than that obtained with other pozzolanic materials, and particularly with metakaolin [9] [45]. The amount of newly formed compounds raises, as aluminates or pozzolanic compounds that favour the increase of the mechanical strength of materials.



**Figure 7.** Effect of temperature on the physicochemical parameters of bauxite: AP: amorphous phases; CH: portlandite; I: strength activity index; SSA: specific surface area; RB: raw bauxite; CB: calcined bauxite.

Finally, it is evidenced that the studied bauxite sample has a significant pozzolanic activity that can be further improved with heat treatment. Bauxite is an interesting material for partially replacing Portland cement in the mixture of concretes. It can be used also in geopolymer formulations that require reactive aluminosilicate species.

## 4. Conclusion

The characterisations of bauxite from Débélé show the presence of mostly alumina hydroxide, but also iron oxide, and silica and titanium oxide are in small quantities. The chemical composition is similar to those of mined bauxites already used in alumina cement and concretes. The sample contains mostly the gibbsite mineral that is an efficient component for the improvement of refractory ceramics since it forms in-situ reactive alumina. The determination of both the amorphous phase content, of the rate of portlandite consumption in an aqueous media, and the strength activity index evidence the high pozzolanic activity. The amorphous phase content can be easily increased by a heat treatment at a relatively low temperature of 600°C. It is an interesting way to improve the behaviour of hydraulic binders as Portland and geopolymers cement. Besides, the properties of refractory ceramics are also improved since the high densification during firing at 1200°C occurs with low linear shrinkage. It is favourable to the production of net-shape refractory ceramics even in the case of large-sized pieces.

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## **Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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