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Potential Applications of Débélé Clays (Guinea): Formulation of Ceramic Compositions and Hydraulic Binders

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Abstract
This study demonstrates the potential uses of two clays collected from Débélé (Guinea). Based on their physicochemical properties, ceramic and hydraulic binder formulations were carried out. The physicomechanical properties of ceramic specimens and cements based on these clays attest to their use in these different fields. Both varieties are suitable for dense ceramic compositions with good dimensional stability on firing. In addition, the melting character of the mineral muscovite, the second main constituent of these clays, contributed to geopolymer gel formation and product compactness. These results also attest to the pozzolanic and amorphous character of Débélé clays, containing over 50% clay minerals, and their application in the formulation of hybrid cements and geopolymer binders.
Key words: Clay, hydraulic binder, ceramic, geopolymer, physicomechanical properties.

1. Introduction
In addition to bauxite, Guinea's main mineral resource, clays occupy a prime position due to their abundance and the many possible applications of these minerals on an industrial scale [1, 2]. This is evidenced by their use as raw materials to manufacture various products, or as additives to a raw material to create or improve the functional properties of new products in response to changing uses [3, 4, 5, 6]. However, despite increasing consumption of manufactured products derived from these minerals, their production remains underdeveloped in some countries, such as Guinea. Indeed, clays, classic raw materials in cement and ceramic matrices, have until now only been exploited for artisanal pottery. Yet these resources can be transformed into basic building materials for walls, roofs and floors, providing a solution to the precarious housing situation that is still a preoccupation in developing countries. Portland cement, the world's most widely used building material since its invention in the 1950s, is still the subject of a great deal of scientific and technical research to improve its properties, durability and cost.
What's more, its manufacture leads to the release of greenhouse gases, which implies a concern for compliance with environmental standards [7, 8]. The partial substitution of a certain quantity of Portland

cement by minerals, when they are available at competitive prices, has proved advantageous, not only from an economic and ecological point of view, but also in terms of product performance [9, 10]. The challenge of optimising compositions and the process needed to manufacture products with satisfactory usage characteristics at minimum production cost also involves the availability and control of raw material characteristics [7, 8]. This is without ignoring the specific case of Guinea, where the development of local resources as a contribution to sustainable development is a permanent political concern. For this reason, the availability and easy access to these clay materials on Guinean territory is an opportunity to be seized in order to reduce the cost of transporting manufactured products and to promote job creation. This will help to make the most of these resources in the construction sector and stimulate investment with a view to creating local businesses and industries to exploit these raw materials efficiently, with the potential to reduce the cost of housing. This study presents the potential applications of Débélé clays in ceramics, hybrid cement and ecological or geopolymer cement. Ceramic formulation tests are being carried out to assess the possibility of using these clays in this field. Hybrid cement formulations, in which 20% by mass of portland cement is substituted by raw clay calcined at 600°C and geopolymer cement, are also being carried out. Clay powders activated at 600, 700 and 800°C were used for this purpose. The physicomechanical properties of all the ceramic, hybrid cement and geopolymer specimens were evaluated and compared with standard norms.

2. Materials and methods

2.1 Materials

The two clays (Figure 1) used in this work come from Débélé, Kindia prefecture (Republic of Guinea). They are named ABD and ARD respectively because of their colour; the former is white and the latter reddish [11].

Figure 1: Aspects of raw clay samples from Débélé (Kindia, Guinea)

The physicochemical and mineralogical characterisation of the samples, previously determined, are presented in Table I [11, 12, 13].

Table I: Physicochemical and mineralogical characteristics of clays

Components	*ABD*	*ARD*
Physical parameters		
Absolute density (g/cm^3)	2.4	2.5
Active specific surface area (m^2/g)	42.2	23.3
Mass (mg) of CH fixed per 1g of sample activated at 600°C	1107.4	796.2
Amorphous phase content of powders activated at 600°C (%)	71.9	63.5

Mechanical activity index of powders activated at 600°C (%)	93.5	88.1
Linear shrinkage on firing at 1200°C (%)	4.5	3.8
Plasticity index	25	23
Clay phase: $2<\Phi< 20$ µm	51.6	48.5
Clay phase: $\Phi < 2$µm (%)	48.5	51
Chemical composition		
SiO_2	52.40	51.20
Al_2O_3	30.90	30.40
Fe_2O_3	1.80	3.70
K_2O	5.90	4.80
TiO_2	1.60	1.60
MgO	0.50	0.40
CaO	0.10	0.10
Na_2O	0.20	0.10
P_2O_5	0.10	0.10
Cr_2O_3	0.02	0.02
SO_3	0.13	0.030
MnO	<0.01	<0.01
LOI	6.20	7.50
Total	99.74	99.96
Mineralogical composition (%)		
Kaolinite	57.4	55.1
Muscovite	27.0	19.9
Quartz	11.3	18.3
Hematite	1.8	/
Anatase	1.6	1.6
Gibbsite	0.6	0.5
Goethite	/	4.6
Total	99.70	100.00

2.2 Method

The ABD and ARB clay powders obtained by 75 µm wet sieving and drying were used to make the ceramic specimens, hybrid mortars and geopolymer pastes. The ceramic specimens are shaped using a laboratory hydraulic press, using 2 g and 50 g of mixture moistened with 2% water. This mixture is homogenised and poured into the corresponding mould to be compacted using a hydraulic press at a pressure of 0.4 KPa for the pellets and 0.7 KPa for the parallelepiped wafers. These specimens were then dried at room temperature (25°C) in the laboratory for 24 hours before undergoing heat treatment in a muffle furnace to be baked at 700, 800, 900, 1000 and 1100°C respectively. Hybrid mortars are formulated by substituting 20% by weight of portland cement with raw clay powders calcined at 600°C of each of the varieties with a water/cement ratio (W/C) of 0.6. The mixture was introduced into a CONTROLAB automatic mixer (MIX MATIC) in accordance with standard NF EN 196-1. The geopolymer binders were also formulated with the two types of clay by mixing the powders activated at 600, 700 and 800°C with the liquid precursor in a solid/liquid (S/L) weight ratio equal to 1.20 for ABD and 1.11 for ARD. All the specimens: ceramics, mortars and geopolymers were subjected to various physical tests: apparent density, water absorption rate, open porosity and mechanical tests: compressive strength for mortars and geopolymers, flexural strength for ceramics in accordance with standard norms [14, 15, 16].

3. Results and discussion

3.1 Characteristics of the ceramic specimens

The firing products of the clays all have a smooth appearance whatever the temperature, which means that they are well vitrified and less porous. In addition, the specimens of both clays retain a light colour, which can be modified if necessary by adding colouring oxides (Figure 2).

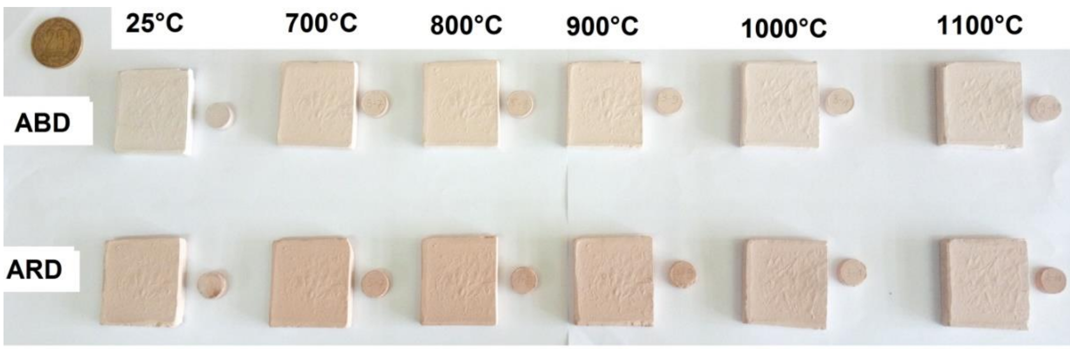

Figure 2: Appearance of specimens before and after firing

After heat treatment between 700 and 1100°C, these specimens have properties close to those of vitrified ceramics (Figure 3): density varies from 2.1 to 2.5 g/cm^3 for ABD and from 1.5 to 1.8 g/cm^3 for ARD; open porosity decreases from 24.8 to 10.7% for ABD and from 34 to 14.7% for ARD with a consequent water absorption rate that varies from 12.7 to 8.6% and from 17.4 to 11.7% for ABD and ARD respectively; flexural strength increases from 7.2 to 20.1 MPa for ABD and from 5.3 to 14.8 MPa for ARD [17, 18, 19]. Another factor to take into account is the contribution of fine quartz particles, which dissolve earlier in the viscous flow. The effect of these fine particles on the densification process remained lower than that of kaolinite and muscovite. This is consistent with the higher densification rate in ABD with its high clay mineral content (Table I) compared to ARD. The characteristics and properties of the ceramic compositions obtained confirm the fluxing nature of the two clays; parameters necessary for obtaining vitrified ceramics [4, 20, 21, 22, 23].

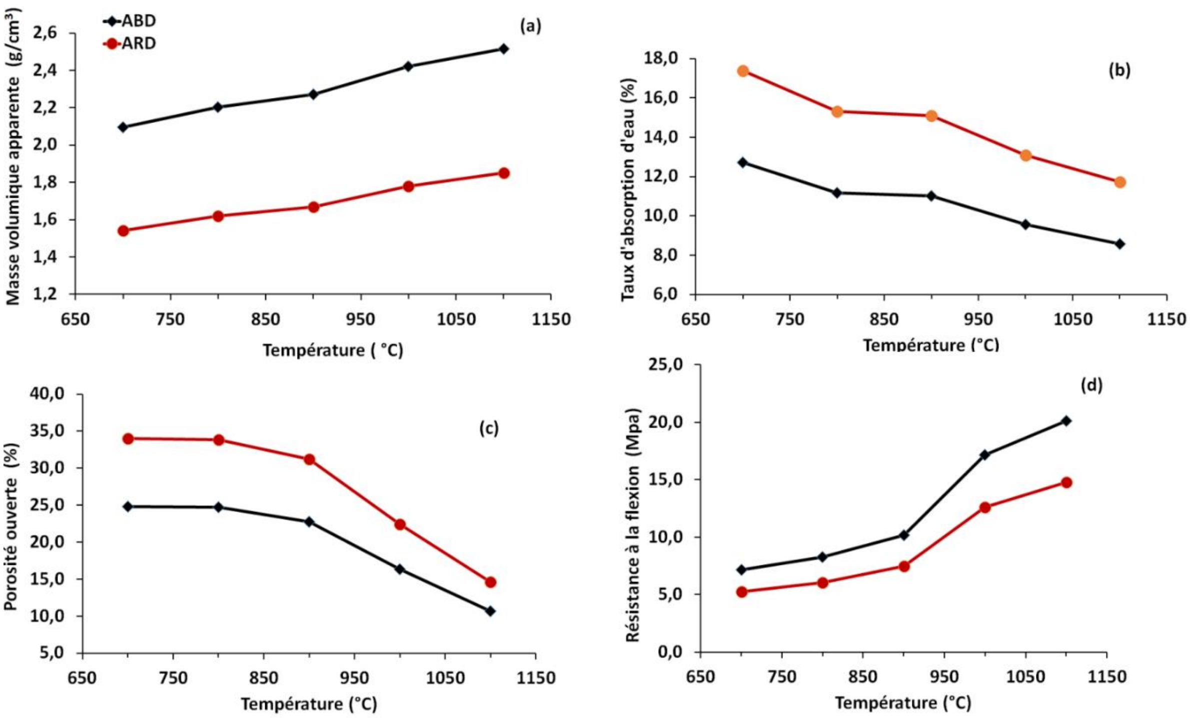

Figure 3: Changes in physical properties as a function of firing temperature.

3.2 Physicomechanical properties of mortars

Various physicomechanical characterisation tests were carried out on mortar specimens (Figure 4) in the hardened state at 7, 28, 45 and 90 days. Expressed as a percentage, the average values for open porosity (π) and water absorption rate (W) are shown in Figure 5. A decrease with age in these parameters is generally observed. Porosity ranged from 21 to 13.80% and water absorption from 11.20 to 5.24%.

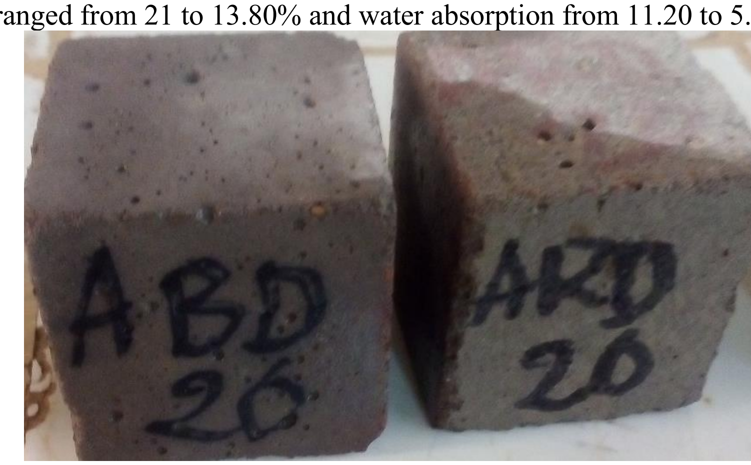

Figure 4:: Appearance of ARD and ARD clay-based mortar specimens

Furthermore, it appears that the first few days of curing are the most important in terms of water absorption, which decreases over time. This finding is related to the porosity and the higher degree of reactivity of the calcined forms. It is also in line with the level of CH fixed as observed in the Modified Chapelle Test. The decrease in pore density and water absorption rate is explained by the chemical activity (hydration) leading to accelerated formation of secondary hydrates, CSH, which result in the filling of pores between particles within the matrix [24, 25, 26, 27].

In addition, the decrease in π and W with specimen age provides a means of predicting the mechanical performance (Figure 6) and durability of formulated mortars [28, 29]. Analysis of the test results for apparent density (ρa) and compressive strength (Rc) shows a slight change in ρa and Rc with the age of the specimens. In both series of mortars, the density varies between 1.8 and 2 g/cm^3 and the overall strength varies between 15 and 43.65 MPa. While the apparent density of the hybrids remains lower than that of the control mortar, their mechanical strength has increased significantly**.** In fact, for powders calcined at 600°C, the strength of these hybrids is greater than that of the control from the age of 45 days. This behaviour is related to the pozzolanicity index (Table I) of the clays, which favours cement hydration and the intensification of chemical reactions thanks to the consumption of portlandite. As a result, additional hydrates, CSH, are formed and precipitated, which are responsible for the long-term compactness of the matrix [27, 30, 31].

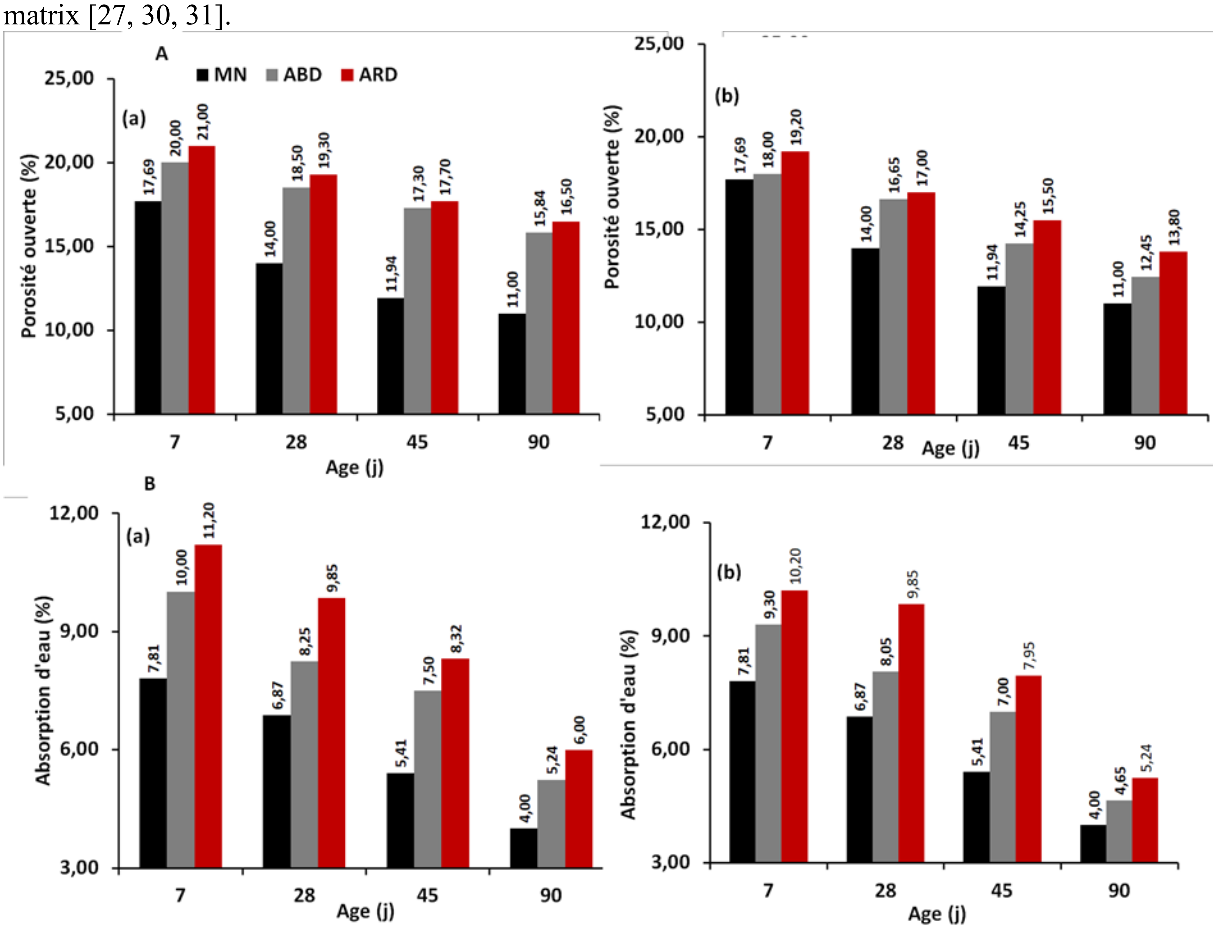

Figure 5:: Changes in open porosity and water absorption as a function of mortar age: (a & c) raw clay-based; (b & d) calcined clay-based.

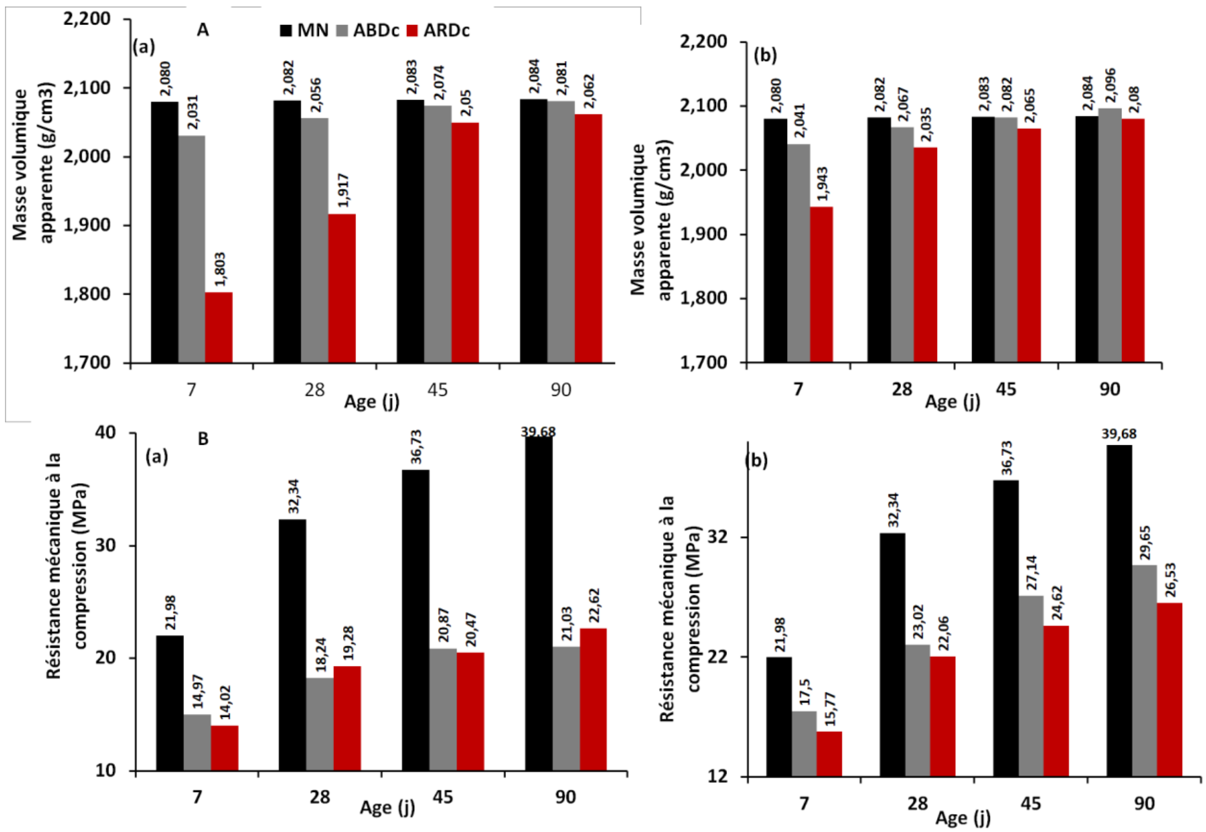

Figure 6: Development of bulk density (ρa) and compressive strength as a function of age of mortars: a) based on raw clays; b) based on calcined clays.

It can be concluded that the development of the density and mechanical strength of the products correlates well with the chemical/mineralogical composition, the amorphous phase content, the mass of CH fixed and the mechanical activity index recorded in Table I. This behaviour is also due to the pozzolanic characteristics of calcined clays. This behaviour is also due to the pozzolanic characteristics of calcined clays [30, 32]. For example, calcined clay-based hybrids are suitable for masonry applications in contact with aggressive environments (waste water, soil, seawater, etc.) in accordance with Belgian standard NBN EN 1052-1, which requires a strength of 20 MPa [33, 34, 45].

3.3 Physicomechanical properties of geopolymer binders

The appearance of geopolymer binder specimens on demoulding and at day 42 is illustrated in Figure 7. These specimens are characterised by the absence of any surface defects such as efflorescence, a common phenomenon in aluminosilicate-based geopolymers [36, 37].

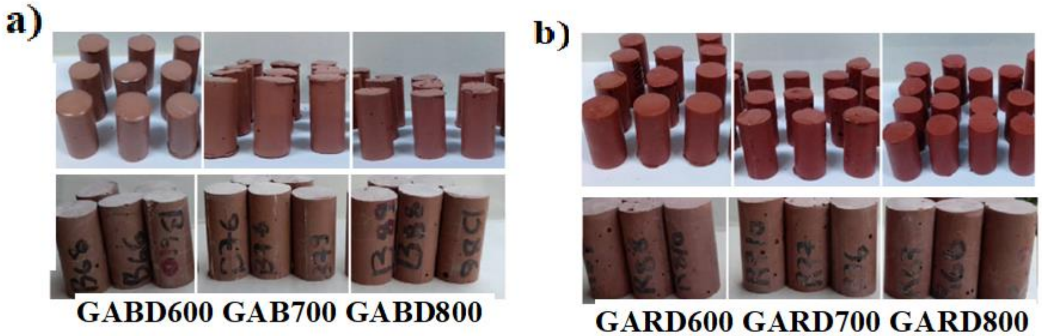

Figure 7: Appearance of geopolymer specimens

The absence of efflorescence is due to the rapidity of the dissolution rate, which does not favour infiltration of CO2 from the air into the geopolymer matrix. In addition, the specimens retained their shape from demoulding through to the test periods, a sign of good consolidation and a good seal, confirming their stability over time. In addition, the activation temperature of the powders had a remarkable effect on the development of the apparent density (Figure 8A) of the binders obtained, which increased with the age of the specimens. The density of GABD binders varies between 2.92 and 2.47 cm^3 and that of GARD binders between 1.86 and 2.16 cm^3.

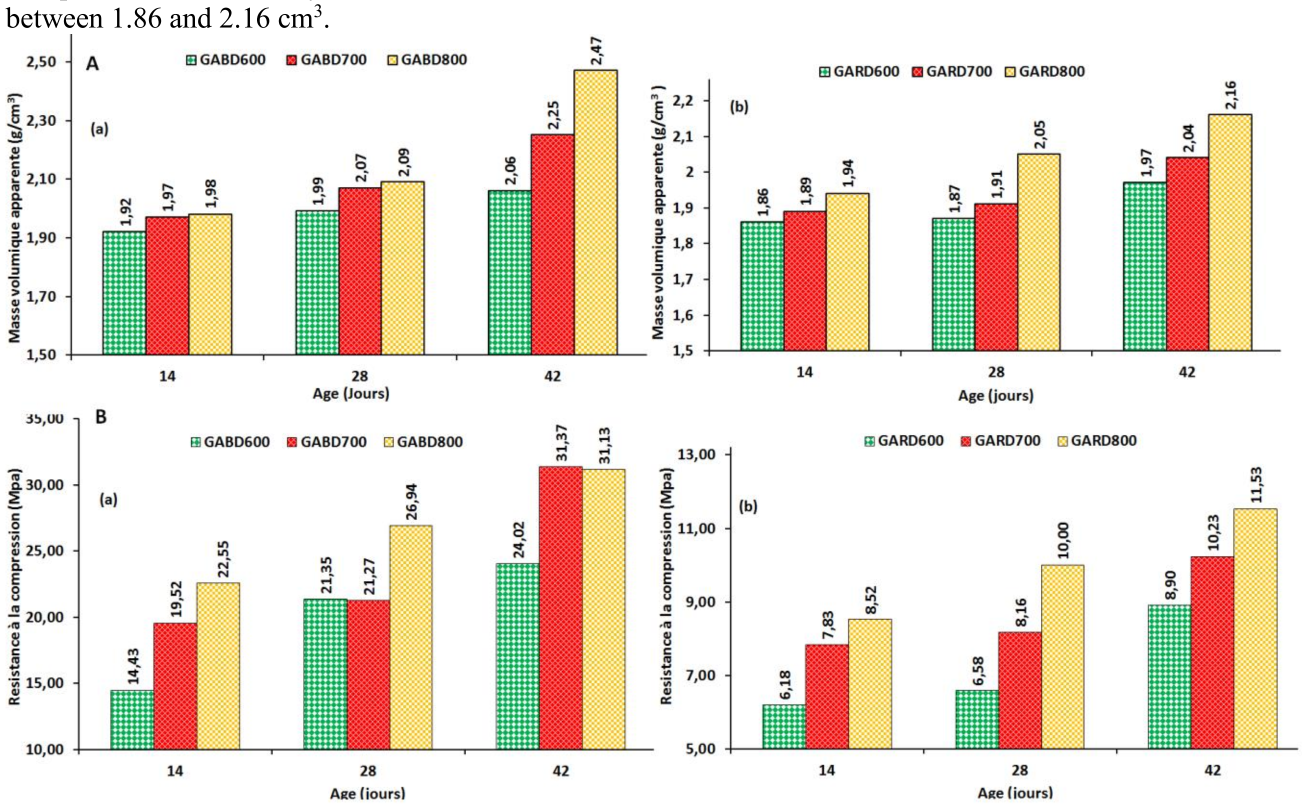

Figure 8: Apparent density (A) and mechanical compressive strength (B) as a function of age for a) GABD and b) GARD specimens.

As a result, the products are denser in the first case than in the second. In fact, the geopolymerisation process is more intense in ABD-based formulations containing the highest proportions of kaolinite and muscovite (Table I). These minerals therefore contributed favourably to densification and the development of mechanical performance (Figure 8B) [38, 39]. Specimens from the GABD series have the best mechanical performance, varying between 14.43 and 31.37 MPa, while those from the GARD series oscillate between 6.18 and 11.56 MPa. In short, the amorphous phase content and thermal transformation of muscovite as a flux mineral have played a largely favourable role in the development of mechanical strengths, which are acceptable for certain applications, as demonstrated by the work of Yang et al. [40].

4. Conclusion

The aim of this work was to experiment with the application of two varieties of clay from Débélé (Guinea) in ceramic compositions and the formulation of hydraulic binders. The results obtained showed the following:

- ✓ the ceramic specimens based on the two clays treated between 700 and 1100°C have properties close to those of vitrified ceramics: bulk density greater than 2 g/cm^3 for ABD and greater than 1.5 g/cm^3 for ARD ; open porosity decreases from 24.8 to 10.7% for ABD and from 34 to 14.7% for ARD with a consequent water absorption rate that varies from 12.7 to 8.6% and from 17.4 to 11.7% for ABD and ARD respectively; flexural strength increases from 7.2 to 20.1 MPa for ABD and from 5.3 to 14.8 MPa for ARD. In addition, the specimens of the two clays retain a light colour, which can be modified if necessary by adding colouring oxides;
- ✓ the substitution of 20% by mass of portland cement by raw clay powders calcined at 600°C for the formulation of mortars shows that these additions are chemically active mineral additives. All the physico-mechanical properties of hybrid mortars show acceptable values and normal development.: reduction in porosity and water absorption on the one hand, and development of the apparent densities and mechanical strength of the specimens on the other. With a minimum mechanical strength of 15 MPa at the youngest age, it offers a wide range of masonry applications in the formulation of less expensive hydraulic binders as provided for in technical standards for the construction of buildings and other structures;
- ✓ the specimens of geopolymer binders obtained show good consolidation from demoulding, which continues with age. On the 42nd day, depending on the activation temperature of the precursors, the specimens had an apparent density of between 2.06 and 2.47 g/cm^3 for GABD and between 1.97 and 2.16 g/cm^3 for GARD, with decreasing porosity favouring appreciable development of the mechanical compressive strength, with a minimum of 11.53 MPa and a maximum of 31.37 MPa. Muscovite, a fluxing mineral, has contributed to the increase in amorphous rates and to the geopolymerisation process. These products can therefore be used as construction materials for structures where waterproofing is required.

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