VALORISATION OF CLAY MINERALS FROM THE DEPARTMENT OF BOYACÁ (COLOMBIA) FOR THE PRODUCTION OF VITRIFIED CERAMIC MATERIALS

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ABSTRACT

This study has allowed the technical and scientific potential to be studied of clay materials from the Department of Boyacá, in particular from the municipalities of Sogamoso, Ráquira, and Cómbita, by the ceramic characterisation of these materials. This has provided extensive knowledge of these clays, with the prospect of providing them with greater added value. The instrumental characterisation focused on the following tests: mineralogical analyses by X-ray diffraction (XRD); chemical characterisation by X-ray fluorescence (XRF); and evaluation of physico–ceramic properties such as linear shrinkage, porosity, and mechanical strength. This was considered key information for the development of possible applications in the field of science and ceramic technology.

1. INTRODUCTION

Colombia is an emerging economy with great economic potential in its regions, as reflected in the ANDI 2012–2013 report, witness a per capita GDP of US\$ 8,127[1]. It is the fourth largest economy in Latin America, after Argentina, Mexico, and Brazil. Consequently, it occupies a key position in fostering investigations aimed at technological development and innovation, which attract great interest for investment as part of government policy. The construction sector in Colombia has witnessed a positive growth trend in the last decade of 7.9%, 6.2% being in building constructions and 5.0% in civil engineering works [1-3]. The latter is significant in view of the country's need for infrastructure development. For this reason, this investigation focused on the study of the geological deposits of Colombia, which are rich in raw materials such as clays, limestone, phosphoric rocks, and silica sands, among other minerals, which could be used for manufacturing structural ceramic products for construction. The study is focused on promoting the economic development of regions such as the Department of Boyacá, the centre of interest in this investigation, this being part of the policy for improvement of the productivity and competitiveness of the mining sector, in which it is sought to increase the participation of investors, attracting technical resources with national and international capital to provide the mining production chain with greater added value. The importance is therefore to be highlighted of this investigation, which has allowed clay materials from the Department of Boyacá, in particular from the municipalities of Sogamoso, Ráquira, and Cómbita, to be characterised, in order to analyse the potential of these materials from a technical-scientific perspective.

2. EXPERIMENTAL

In regard to the geological formation that generated the region of Boyacá, this Colombian region is characterised by a predominance of outcrops of sedimentary rock and folds from the Cretaceous period, consisting of lutite and sandstone, as well as compact rocks such as limestone, this being predominant in the towns of Sáchica, Sutamarchán, Moniquirá, Paipa, Duitama, and Sogamoso [4,5]. In contrast, the rocks from the upper Tertiary period, consisting of yellow, grey, and greenish clays, iron ore and gypsum, are located in Sogamoso and Paz del Río. Taking into account these formations, clay minerals were collected from the regions of Sogamoso, Ráquira, and Cómbita for the present investigation (Figure 1).





Figure 1. Geographic location of the Department of Boyacá (Colombia).

All the clays detailed in Table 1 were analysed in the Laboratories of the Central Service for Scientific Instruments of Universitat Jaume I of Castellón (Spain), in close collaboration with the company Tierra Atomizada, S.A., and the ceramics college Escuela Superior de Cerámica, these last two being located in L'Alcora (Spain). The following instrumental analyses were conducted on each of the clays: mineralogical characterisation by X-ray diffraction (XRD) with a Bruker AXS model D4 Endeavor diffractometer; chemical characterisation by X-ray fluorescence (XRF) with a Bruker S4 Pioneer sequential spectrometer; simultaneous thermal analysis (DTA/TG) with a Marc-BAHR model STA 503 thermo-analyser. The clays were physically and chemically characterised by testing their plasticity using the Pfefferkorn method, after-pressing expansion, water absorption, and dry and fired linear shrinkage. Their vitrification curves were also determined and, finally, particle size distribution was determined by the laser diffraction method (Coulter LS32).

DESIGNATION	DESIGNATION
SOGAMOSO1	COMBITA 4
SOGAMOSO 2	COMBITA 5
SOGAMOSO 3	RÁQUIRA 1
CÓMBITA 1	RÁQUIRA 2
CÓMBITA2	RÁQUIRA 3
CÓMBITA 3	RÁQUIRA 4

Table 1. Nomenclature of the clay minerals from the Department of Boyacá (Colombia).

3. RESULTS AND DISCUSSION

3.1. MINERALOGICAL ANALYSIS BY X-RAY DIFFRACTION

The diffractograms obtained using the X´Pert High Score Plus software for XRD data analysis are shown in Figures 2 to 4. The qualitative mineralogical characterisation indicates that all the clays from the Department of Boyacá (Colombia) exhibited diffraction peaks corresponding to Quartz, (α -SiO₂), as well as clay fractions corresponding to kaolinites. The clays from the Ráquira sector also contained pyrophyllites, montmorillonites, and feldspars.



Figure 2. Diffractograms of the Sogamoso clays.



Figure 3. Diffractograms of the Cómbita clays.





Figure 4. Diffractograms of the Ráquira clays.

3.2. CHEMICAL COMPOSITION

In accordance with the chemical analysis performed by X-ray fluorescence, the characteristic composition of the clays used in this investigation is shown in Table 2.

DESIGNATION	Na ₂ O	MgO	Al_2O_3	SiO ₂	P_2O_5	SO ₃	K ₂ 0	CaO	TiO ₂	MnO	Fe ₂ O ₃	L.O.I.
SOGAMOSO1	0.02	0.64	19.79	56.63	0.31	0.99	1.78	0.21	1.03	0.02	7.62	10.98
SOGAMOSO 2	0.09	0.42	18.76	65.95	0.12	0.02	0.79	0.16	0.65	0.00	2.45	10.66
SOGAMOSO 3	0.09	0.17	11.87	80.07	0.04	0.06	0.31	0.10	0.54	0.00	0.87	5.96
COMBITA 1	0.21	0.22	21.81	56.90	0.11	0.13	0.97	0.19	1.09	0.01	4.56	14.02
COMBITA2	0.18	0.21	26.99	59.02	0.09	0.03	1.23	0.04	1.27	0.00	0.83	10.29
COMBITA 3	0.28	0.44	22.09	60.90	0.07	0.07	1.02	0.17	0.95	0.01	4.65	9.63
COMBITA 4	0.40	0.17	15.41	73.84	0.11	0.03	0.60	0.05	1.24	0.00	2.60	5.95
COMBITA 5	0.15	0.32	18.23	69.68	0.11	0.02	0.80	0.11	0.88	0.00	2.86	7.00
RAQUIRA 1	0.14	0.16	20.73	63.47	0.13	0.03	0.79	0.10	1.19	0.00	4.56	8.85
RAQUIRA 2	0.28	1.16	20.72	55.99	0.12	0.07	1.49	0.81	1.00	0.03	7.53	11.08
RAQUIRA 3	0.24	0.37	17.21	67.75	0.14	0.04	1.08	0.13	0.81	0.03	5.67	6.76
RAQUIRA 4	0.09	0.34	24.16	57.80	0.16	0.03	0.61	0.15	1.18	0.01	3.99	11.57

Table 2. Characteristic chemical composition of the clays from the Department of Boyacá (Colombia).LOI = Loss on ignition.

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Taking into account the mineralogical results and the chemical composition, the Sogamoso 1, Combita 1 and 2, and Ráquira 1 clays were discarded because they displayed similar properties. They were therefore not considered in the subsequent studies.

The predominant minerals in each of the selected clays for the further characterisation study are highlighted in Table 3.

SAMPLE	GENERAL CHARACTERISTICS	SAMPLE	GENERAL CHARACTERISTICS			
SOGAMOSO2	KAOLINITIC	CÓMBITA5	KAOLINITIC			
SOGAMOSO3	REFRACTORY	RÁQUIRA2	KAOLINITIC			
CÓMBITA3	NON-PLASTIC	RÁQUIRA3	NON-PLASTIC			
CÓMBITA4	KAOLINITIC	RÁQUIRA4	KAOLINITIC			

Table 3. Clays from the Department of Boyacá (Colombia) selected for their ceramic properties.

The (dry) texture of the clays as they were observed, without previous milling and sieving treatment, is shown in Figure 5.



Figure 5. Colombian clays from Boyacá selected for their ceramic properties.

3.3. CERAMIC CHARACTERISATION

The results of the most noteworthy physico-chemical properties that were determined are shown in Figure 6.



Figure 6. Vitrification curves of the Colombian clays from Boyacá.





Figure 7. Ráquira3 at 1165°C.



Figure 8. Sogamoso3 at 1165°C.



Figure 9. Cómbita3 at 1165°C.



Figure 10. Cómbita4 at 1165°C.



Figure 11. Cómbita5 at 1165°C.

Figure 7 shows the colour produced by the Sogamoso2 clay at 1165°C, the temperature at which it exhibited maximum linear shrinkage (2.4%), corresponding to a water absorption of 7.8%. These are typical values for refractory clays, just as the plasticity, which exhibited a low value (17.4% PI). Dry mechanical strength was 4.2 N mm⁻², a moderate value for a clay.

Figure 8 shows the colour produced by the Sogamoso3 clay at 1165°C, with a linear shrinkage at this temperature of 6.65%, corresponding to a water absorption of 3.70%. It displayed a high plasticity index (22.8% PI) and a dry mechanical strength of 5,8 N mm⁻².

Figure 9 shows the colour produced by the Cómbita3 clay at 1165°C. It exhibited very stable thermal-dimensional behaviour between 1115°C and 1165°C, with a linear shrinkage of the order of 1% and a minimum water absorption (9.2%) at 1165°C, reflecting properties of a refractory clay. Its plasticity was 20.3% PI, with a dry mechanical strength of 5,9 N mm⁻².

Figure 10 shows the colour produced by the Cómbita4 clay at 1165°C in the range of temperatures between 1115°C and 1165°C of the vitrification curve. It underwent no significant changes, displaying uniform behaviour in both linear shrinkage and water absorption. It was a clay with high shrinkage, and it displayed good plasticity, 23.5% PI, and a mechanical strength of 3,4 N mm⁻².

Figure 11 shows the colour produced by the Cómbita5 clay at 1165°C, with a minimum water absorption at 1165°C and a linear shrinkage of about 5.21%. The linear absorption slope had a pronounced curve between 1120°C and 1130°C, indicating that the material was quite active in this range of temperatures, vitrification onset taking place at 1115°C. Linear shrinkage was stable in the evaluated temperature range. The material exhibited good plasticity, 25.9% PI, with a dry mechanical strength of 4,8 N mm⁻².





Figure 12. Ráquira2 at 1165°C.

Figure 12 shows the colour produced by the Ráquira2 clay at 1165°C in the range of temperatures between 1115°C and 1165°C of the vitrification curve. It underwent no significant changes, though the graph showed a pronounced reduction between 1130°C and 1145°C, it being characterised as a highly refractory material. It had a plasticity of 22.18% PI and a dry mechanical strength of 5,3 N mm⁻².



Figure 13. Ráquira3 at 1165°C.



Figure 14. Ráquira4 at 1165°C.

Figure 13 shows the colour produced by the Ráquira3 clay at 1165°C in the range of temperatures between 1115°C and 1165°C of the vitrification curve. To be noted was its uniform behaviour in linear shrinkage and water absorption. A clay was involved with high shrinkage, a plasticity of 20.8% PI, and a dry mechanical strength of 1,8 N mm⁻².

Figure 14 shows the colour produced by the Ráquira4 clay at 1165°C. During its vitrification curve it reached minimum water absorption at 1165°C (9.36%) with a linear shrinkage of about 2.22%. The linear absorption curve exhibited a pronounced slope between 1140°C and 1165°C, while the linear shrinkage underwent no major changes in the evaluated temperature range. The material displayed good plasticity, 23.2% PI, and a dry mechanical strength of 4,0 N mm⁻².

It may be noted that none of these clays exhibited black core in the organic matter test.



4. CONCLUSIONS

The results obtained allow the following conclusions to be drawn:

The mineralogical analysis of all the studied clays indicated the presence of quartz and clay minerals (kaolinite). In addition, for the clays from Ráquira, montmorillonite, pyrophyllite, and feldspar were also present.

Physico-chemical analysis highlighted the variation in the alumina content for the different clays, which provided them with a kaolinitic character.

Taking into account the vitrification diagrams, the studied clays exhibited appropriate behaviour for use as components in body formulations for traditional ceramics: red-body porosa tile, white-body porosa tile, porcelain tile, and red-body stoneware tile, for the manufacture of ceramic floor and wall tiles.

Finally, in view of the results obtained, the mixture in given quantities of these clays will enable them to be used to formulate quality ceramic bodies. However, depending on the type of product to be manufactured, it may be necessary to add other raw materials such as carbonates, feldspars, calcites, and kaolins, which are also present in the region.

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REFERENCES

- [1] International Monetary Fund. First quarter of 2013.
- [2] Colombia: Balance 2011 y perspectivas 2012. Sector Financiero. ANDI: Asociación Nacional de Empresarios de Colombia. Consulted 15 March 2013.
- [3] Colombia: Balance 2011 y perspectivas 2012. Sector Minero-Energético. ANDI: Asociación Nacional de Empresarios de Colombia. Consulted 15 March 2013.
- [4] Rezoni, G. Mapa Geológico plancha Nº 171, escala 1: 100000. Ingeominas, 1976.
- [5] Plan de Ordenamiento Territorial de Paipa-Boyacá.
- [6] Amorós, J.L., Barba A., Beltrán., Beltrán V. Estructuras cristalinas de los silicatos y óxidos de las materias primas cerámicas. Instituto de Tecnología Cerámica – Asociación de Investigación de las Industrias Cerámicas, 1994.
- [7] Barba A., Beltrán V., Feliu C., García J., Ginés F., Sánchez E., Sanz V., Materias primas para la fabricación de Soportes de Baldosas Cerámicas. Instituto de Tecnología Cerámica, 1997.
- [8] Escribano P., Carda C.J., Cordoncillo E., Esmaltes y Pigmentos Cerámicos. Faenza Editrice Ibérica S.L., Castellón, 2001.
- [9] Sánchez M.L., Carda C.J., Materias primas y aditivos cerámicos. Faenza Editrice Ibérica S.L., Castellón, 2003.
- [10] Restrepo O. J., Barrachina E., Cerisuelo E., Carda J.B., Fabricación de gres porcelánico en Colombia: Una estrategia para el mercado cerámico nacional. Qualicer, 2012.
- [11] Ojoa W., Berdugo C., Alvarado G., y Escobar C. Evaluación geológica minera de las arcillas de Arcabuco. Universidad Pedagógica y Tecnológica de Colombia, Sogamoso (Boyacá), 1992.