STUDY OF CERAMIC BODY COMPOSITIONS WITH THE ADDITION OF MULLITES OBTAINED FROM THERMALLY ACTIVATED CLAYS

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ABSTRACT

This research study was undertaken to develop new products by the thermal activation of kaolinitic clays. Materials from a mining exploration by-product were used for this purpose. These were rejected materials of no value to the mining company, but in which money had been invested to determine their mineralogical, physical, and chemical characteristics. These determinations are performed to establish whether a given material could be supplied or not to different mining clients in the sector. Finding a way to develop new products with high added value by calcination would allow the clay extraction sector to extend its portfolio, using a new mineral processing technology such as calcination.

This research project explores the possible application of this approach in ceramic bodies, specifically in two formulations. One was for vitreous china sanitary ware in which chamotte with high Mullite contents was used, for which three clays calcined at 1400°C were evaluated, and the other was for ceramic tile, for which a clay calcined at 800°C was evaluated.

1. INTRODUCTION

The mining sector exploits and characterises the ground in different regions of Colombia, in search of materials with the necessary potential to supply the industrial sector. In this search for materials, a great variety of clays are identified. However, mining companies are forced to reject certain batches of these materials, in which money has been invested to determine their characteristics, in order meet the specifications agreed with clients.

One of the materials extracted from the crust of the earth in large quantities is clay, which has been used for many years as an industrial mineral with a multitude of applications depending on its properties. Each type of clay has characteristic properties, and they are linked to the formation of the ground, extraction region, structural ordering, pressure, and temperature. These features may lead the exploited material not to meet all the necessary requirements for subsequent use in certain types of industries, as is the case in the fabrication of ceramic bodies, glazes, paints, glasses, animal fodder, pharmaceutical consumables, among others.

At present, the industries that supply the ceramic sector with raw materials are companies that have materials such as kaolinitic clays in their portfolio, these being clays that do not all, by their nature, meet the necessary characteristics for clients. A rejected or discarded material is thus left behind in the mine, which could potentially be used in other sectors. These mining companies have no efficient alternative use for these materials. This rejected material provides no benefits, which has led to this technological attempt to identify the feasibility of producing, on a laboratory scale, thermally activated kaolinitic clays, as a contribution to innovation for mining companies to enable them to enter new markets by application of a technological variant such as clay calcination in their production process.

The scientific motivation for this work was the obtainment on a laboratory scale of mullite from thermally activated kaolinitic clays and the generation of changes in the properties of silico-aluminous materials for applications in ceramic bodies. An environmental motivation was also identified, involving the possibility of using all the extracted materials in the mines, and not returning the clay batches that the mining branch has at present but are currently unattractive for clients, based on the fact that the mining operation consists of several stages, priority factors in all of these being control of the landscape, handling of the vegetation, the ground and the water. In addition, an economic motivation was also identified, involving the need of industries devoted to mining activities to enter new markets and widen their portfolio of materials. In addition, it was sought to provide added value to materials that are currently not marketed.

2. EXPERIMENTAL DEVELOPMENT

To carry out this investigation, the following study phases were programmed:

- Exploration, delimitation, and characterisation of the mining area to be investigated.
- Thermal activation.
- Validation of the calcined materials as chamotte in vitreous china sanitary ware and ceramic tile bodies. To conduct each one of these phases, the experimental route illustrated in Figure 1 was followed.

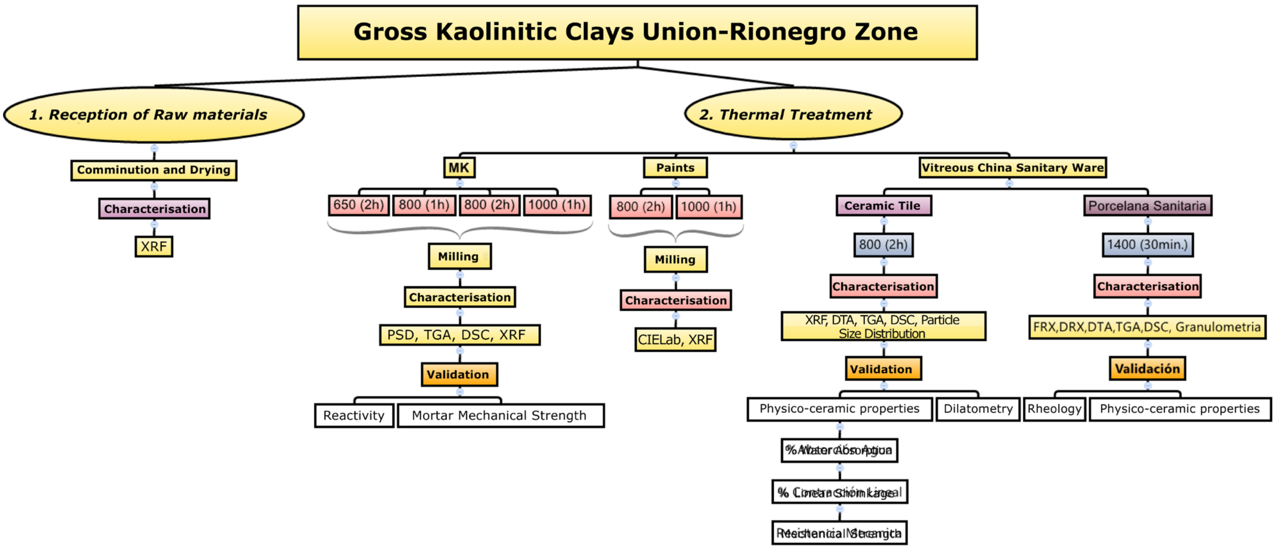

Figura 1. Desarrollo experimental.

2.1 STUDIED MATERIALS

As the scope of the investigation aimed at three fronts, with regard to the validation of clays calcined as mullite, the benchmarks for each possible application were examined and the calcined clays were characterised. The range of clays was thus broken down into each of the different sources.

Clay	Chemical composition (%)								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	P_2O_5	LOI from 110°C to 1000°C
A1	54.30	31.92	0.93	0.30	0.03	0.13	0.84	0.01	11.60
A2	45.68	36.93	0.61	1.33	0.05	0.08	0.09	0.02	14.80
A3	64.28	22.66	0.86	1.11	0.02	0.35	2.75	0.02	7.60
A4	58.71	25.96	1.58	2.06	0.34	0.25	0.25	0.02	10.80

A5	67.56	20.61	3.27	0.26	0.01	0.05	0.34	0.02	7.90
A6	54.30	29.80	1.48	1.49	0.10	0.20	1.13	0.02	11.30
A7	73.44	18.46	0.42	0.24	0.01	0.04	0.45	0.01	6.71
A8	65.39	20.77	4.50	0.26	0.01	0.55	0.73	0.03	7.90
A9	71.14	18.86	0.59	0.27	0.01	0.06	0.37	0.01	7.40
A10	46.30	35.30	0.73	1.57	0.07	0.08	0.13	0.05	15.20

Table 1. Chemical composition and loss on ignition of the clays chosen in the mining exploration phase.

2.2 REFERENCE MATERIALS

The reference material supplied by the company's area for ceramic bodies indicated that the thermal activation conditions needed to be above 1200°C to develop to the mullite phase. Taking this into account, it was decided to use clays A1, A2, and A10 because of their chemical composition and kaolinite content

The ceramic tile bodies were generally a reddish colour, owing to the use of clays with high Fe_2O_3 contents, of the order of 2 to 4%. The clays used in ceramic tiles do not need to be white, as the technical characteristics of the ceramic tiles allow materials formulations to be used that contain impurities. In accordance with Table 1 and Table 5, clay A5 was selected for validation in the ceramic tile. This clay had an Iron content within the range used in ceramic tile bodies (Gueto J.M., 2005).

REFERENCE CHAMOTTE	
Chemical Composition (%)	
SiO_2	45.85
Al_2O_3	49.70
Fe_2O_3	1.35
TiO_2	2.00
CaO	0.07
MgO	0.16
Na_2O	0.03
K_2O	0.22
BaO	0.08
MnO	ND
P_2O_5	0.07
SO_3	ND
LOI from 110°C to 1000°C	0.05

PARTICLE SIZE DISTRIBUTION	
Mesh	Ref. Chamotte
<M325 (%)	34.42
XRF	
Mineral (%)	Ref. Chamotte
Mullite	70-75
Quartz	5-10
Cristobalite	0-5

Tabla 2. Características Chamota referencia para Pasta de Porcelana sanitaria.

3. RESULTS AND DISCUSSION

3.1 THERMAL ACTIVATION

The results of the thermal analysis for each clay that could produce metakaolin at different temperatures are set out below. Figure 2 shows the thermogram of clay A1 without calcining, in which the characteristic kaolinite peak is observed at a temperature of 540°C.

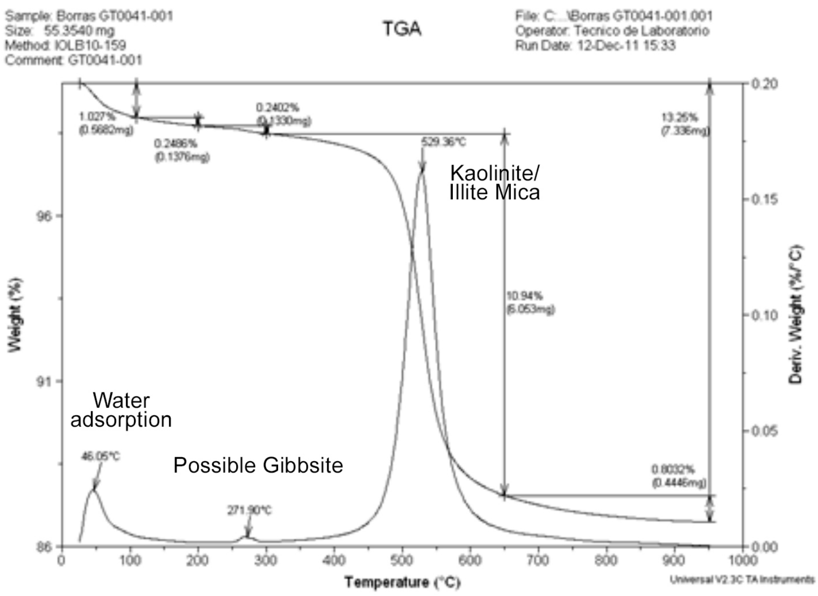

Figure 2. TGA- Clay A1 without calcining.

DTA analysis (Figure 3) displays normal behaviour in the samples at 800°C, showing the mullite peak, indicating the presence of metakaolin in the sample. This peak is not found at 1000°C, which suggests that at this temperature spinel or mullite has already formed in the sample.

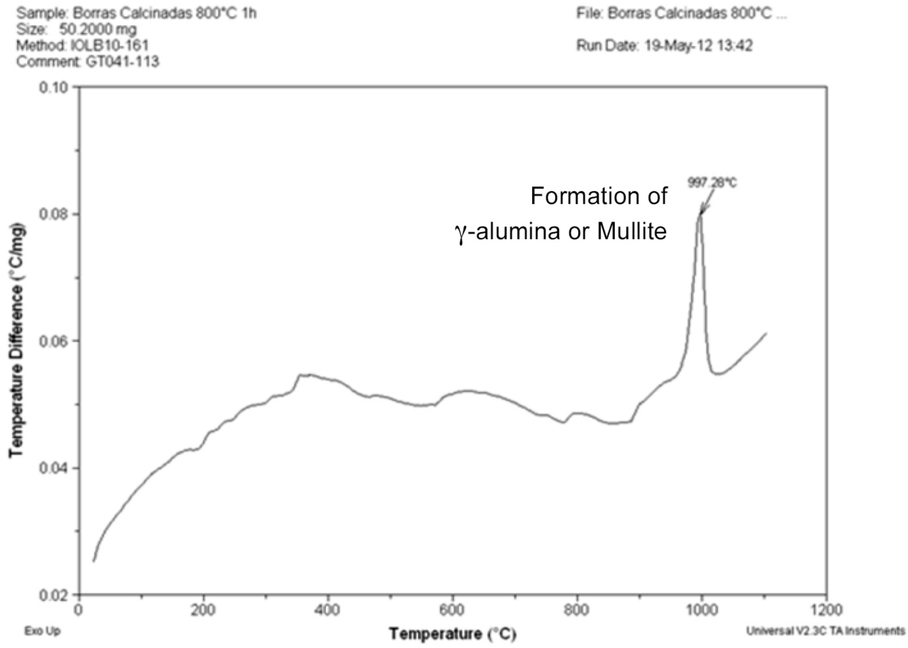

Figure 3. DTA - Clay A1 calcined at 800°C (1 hour).

3.2 CERAMIC TILE

The formulations for ceramic tile, in general, contain plastic materials (Clays), fluxes, and non-plastics (chamotte), which, in the appropriate proportions, provide the finished product with the required technical conditions with regard to water absorption, linear shrinkage, bulk density, mechanical strength, etc. For this investigation, a mixture design (DOE-MIX) was used in which the quantities of certain clays in the formulation were varied, using a fixed quantity of flux, and varying the chamotte content.

For the introduction of the variation conditions of each component in the design, the experience of the area for ceramic bodies of SUMICOL, S.A., played a key part in supplying the necessary information on the role of each material in the formulation, in order thus to use the appropriate ranges for the mixture design.

The chamotte to be validated was replaced in 6 formulations obtained by minitab, varying the chamotte content from 4.7 to 18.77% in the bodies.

3.3 VITREOUS CHINA SANITARY WARE

The results of the thermal analyses performed on the clays calcined at 1400°C for validation in vitreous china sanitary ware bodies are shown below.

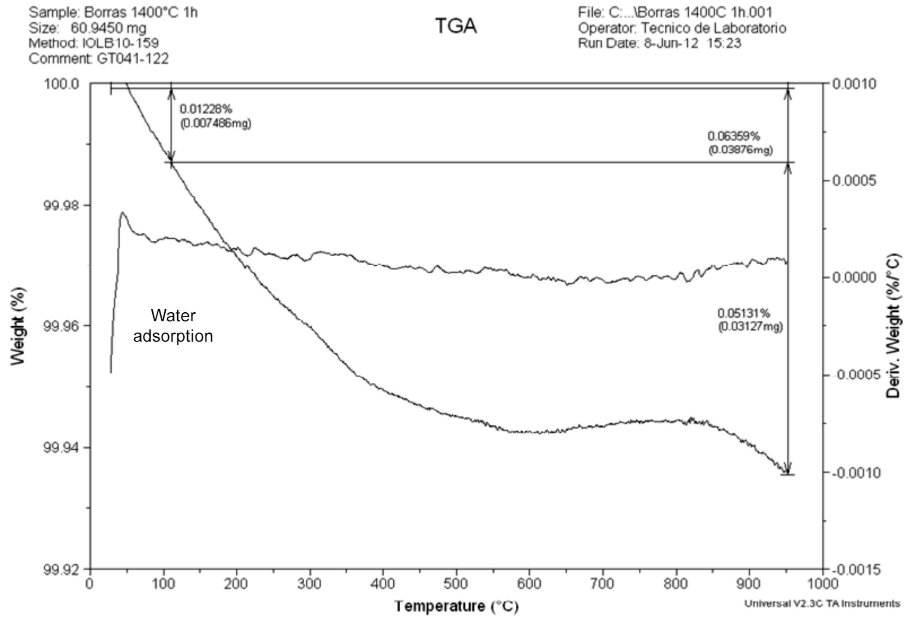

Figure 4. TGA - Clay A1 at 1400°C (30 minutes).

X-ray diffraction (XRD)

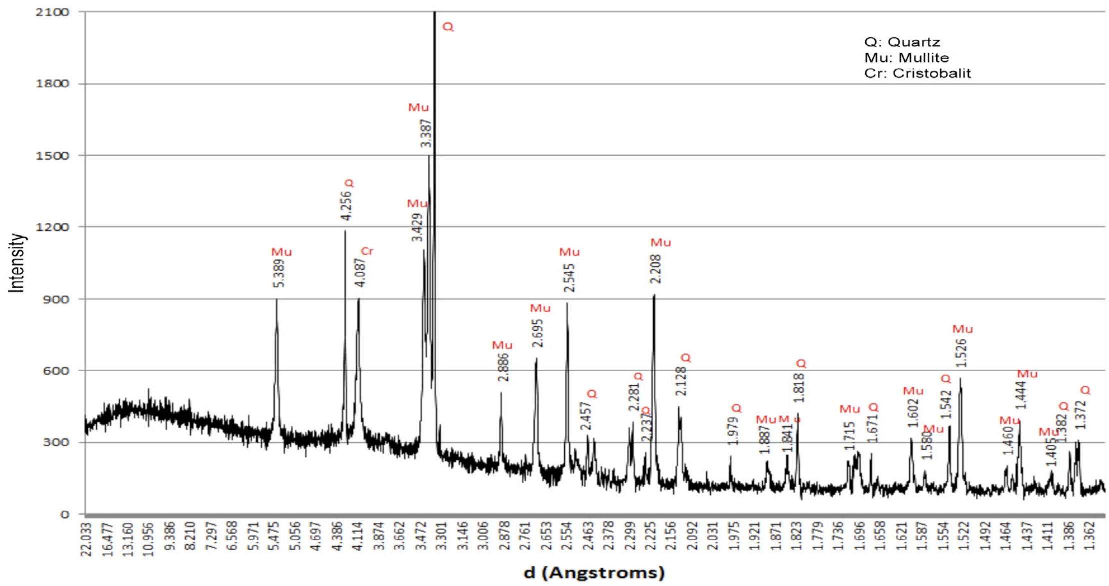

Figure 5. XRD - Clay A1 at 1400°C (30 minutes).

According to the X-ray diffraction analysis performed on the clays calcined at 1400°C, the presence of mullite, quartz, and cristobalite was found as a common factor in the three clays.

3.4 VALIDATION OF THE CERAMIC BODIES

The results obtained of the validation of the chamotte in the ceramic tile and vitreous china sanitary ware bodies are set out below.

3.4.1 Ceramic tile body

The validation was performed by a mixture design of extreme vertices, a replica in the centre, and no replicas in the vertices. Table 3 shows the mixture design obtained by minitab.

C1	C2	Pt type	Blocks	Clay	Arcillolite	Chamotte
3	1	1	1	28.2%	0.0%	18.8%
5	2	0	1	30.5%	4.7%	11.7%
4	3	1	1	32.8%	9.4%	4.7%
6	4	0	1	30.5%	4.7%	11.7%
2	5	1	1	42.2%	0.0%	4.7%
1	6	1	1	18.8%	9.4%	18.8%

Mixture design for chamotte validation in the RV (ceramic tile) body.

Altogether, minitab produced 6 formulations and the reference body was added that is currently used in the RV (ceramic tile) plant of the Corona Organisation.

According to column two of Table 3, the bodies were designated P1, P2 and so on according to the continuing order.

On analysing Table 3, it may initially be concluded that the bodies with the greatest chamotte content (18.8%) required more milling time, just as the body with high clay content. This is because, as the chamotte is a calcined material, it exhibits a greater degree of agglomeration. For the body with a high clay content, as this was very fine, this generated a monosize in the particle size distribution of the body, leading to poor packing and not producing sufficient friction between the particles to reduce particle size, which is ultimately what milling is intended to do.

In terms of compaction, all the evaluated bodies displayed a lower bulk density than the reference body. This is not advisable because it entails a reduction in mechanical strength, which was corroborated by the low breaking load of the 6 evaluated bodies.

The bodies were fired at three temperatures, which are about the temperatures used in the ceramic tile manufacturing process. In the firing stage there was a significant deterioration of bulk density, which came from the green body, a phenomenon that was observed to a greater extent for bodies P1 and P6, these being formulations with the greatest quantity of chamotte.

Two important parameters for the ceramic tile bodies are water absorption and linear shrinkage. The P1, P2, P4, and P6 bodies displayed values far removed from those of the standard body for these two properties, whereas those of bodies P3 and P5 were closer to those of the reference body at all evaluated temperatures. These were the bodies that contained the smallest quantity of chamotte in the formulation.

According to the evaluated bodies, the A5 clay calcined at 800°C for two hours can be introduced as a non-plastic material in a percentage of 4.7% or less. The P3 formulation displayed the most similar physico-ceramic conditions to those of the standard body.

3.4.2 Vitreous china sanitary ware

For the validation of the three chamottes, the product being studied in this investigation, each was alternately replaced in the vitreous china sanitary ware formulation with the reference chamotte.

In the case of the evaluated vitreous china sanitary ware formulation, this is used for the manufacture of large-sized pieces, so that low shrinkage and pyroplastic deformation are required in firing. To achieve this, non-plastic materials must be introduced, such as chamotte. For this investigation, silico-aluminous materials were available that, calcined at temperatures above 1200°C, generated Mullite which, on being added to the body, owing to its needle-like structure, generated a network that increased the mechanical strength of the bodies.

Table 4 reports the results of the fired properties for the vitreous china sanitary ware body made with chamotte produced at 1400°C.

Ceramic Tile Body	Reference	P1	P2	P3	P4	P4	P6
SLURRY							
Milling time in alcohol (min)	27	37	32	30	32	49	57
Residue >M270 (%)	9.16	10.76	0.22	10.84	9.02	10.44	12.24
Residue >M325 (%)	13.52	13.08	14.12	13.20	13.98	14.12	17.04
COMPACTION							
Pressing moisture content (%)	5.92	6.00	5.91	6.19	6.16	6.13	6.14
Pressing pressure (kg/cm^2)	260						
Density (g/cm^3)	2.007	1.884	1.914	1.974	1.909	1.989	1.858
After-pressing expansion (%)	0.60	0.67	0.68	0.59	0.63	0.63	0.77
Drying shrinkage (%)	0.13	0.10	0.14	0.15	0.08	0.17	0.10
Dry thicknesses (mm)	6.98	7.00	7.01	7.01	7.02	7.03	7.05

Breaking load (kg)	9.67	7.79	7.03	8.87	5.65	7.90	6.41
FIRING – Pirometrol kiln							
Time at peak temperature (Min.)	2						
Temperature (ºC)	1100						
Density (g/cm^3)	1.825	1.743	1.759	1.805	1.758	1.805	1.723
Shrinkage (%)	0.61	0.75	0.68	0.59	0.74	0.64	0.56
Water absorption (%)	17.43	20.22	19.62	17.72	19.52	17.78	20.4
Loss on ignition (%)	11.38	10.13	10.71	10.87	10.49	11.63	9.85
Breaking load (kg)	5.21	39.0	43.03	49.63	45.00	47.43	40.2
Time at peak temperature (Min.)	2						
Temperature (ºC)	1115						
Density (g/cm^3)	1.830	1.755	1.770	1.813	1.774	1.812	1.736
Shrinkage (%)	0.84	0.95	0.91	0.79	0.91	0.77	0.89
Water absorption (%)	16.87	19.77	19.10	17.44	18.81	17.51	20.01
Loss on ignition (%)	11.43	10.13	10.75	10.75	10.48	11.62	9.89
Breaking load (kg)	60.83	46.20	45.60	57.17	51.07	48.90	43.83
Time at peak temperature (Min.)	2						
Temperature (ºC)	1130						
Shrinkage (g/cm^3)	1.889	17.66	1.788	1.832	1.798	1.829	1.755
Density (%)	1.05	1.24	1.21	1.07	1.31	1.07	1.18
Water absorption (%)	16.22	19.01	18.33	16.53	17.82	16.80	19.02
Loss on igni-tion(%)	11.39	10.07	10.87	10.96	10.40	11.72	10.18
Breaking load (kg)	70.7	48.30	54.60	62.57	64.97	59.27	49.1

Table 4. Results of the ceramic tile (RV) bodies.

Vitreous china sanitary ware body		Reference	P1	P2	P3
(%) Water absorption		8.42	11.28	10.92	9.67
(%) Shrinkage	Drying	1.67	1.71	1.73	1.66
	Firing	4.02	3.91	3.72	4.32
	Total	5.62	5.56	5.38	5.90
Pyroplastic deformation (cm^{-1})		7.66	6.75	6.68	6.67
Black core		None	None	None	None
Mechanical strength (kg/cm^2)		292.68	297.99	280.12	304.69

Table 5. Results of the vitreous china sanitary ware bodies.

Each prepared body corresponded to the replacement of each chamotte product being studied in this investigation.

According to Table 5, bodies P1, P2, and P3 displayed a higher water absorption than the reference body. However, the technical specifications for the type of prepared body was between 8 and 12%. The linear shrinkage for the three evaluated bodies was very close to that of the reference body.

Pyroplastic deformation is a critical variable in this type of body because the body is used to make pieces with complex designs. When the pyroplastic deformation is reduced to levels like those exhibited by the three evaluated bodies, finished product quality is enhanced.

Bodies P3 and P1 increased the mechanical strength of the reference body.

4. CONCLUSIONS

This investigation allowed kaolinitic clays, which had been rejected by a mining sector company and were not used, to be characterised, and this material to be provided with added value on being thermally activated and finding possible uses in the ceramic, paint, and construction sectors.

Studying the effect of temperature, the variations in exposure times, and the differences in chemical and mineralogical composition of the kaolinitic clays enabled the appropriate conditions to be identified to generate a potential use of the studied clays in different applications.

This investigation allowed materials to be designed, in the case of the validation of chamottes. The material was not just thermally activated, but, thanks to this study, the appropriate milling conditions and particle size distribution for validating the calcined material in ceramic bodies were determined. Several requirements must be met for a material to be included in a formulation and, by an appropriate study, one formulation was obtained for ceramic tile and three formulations were obtained for vitreous china sanitary ware.

This study sought to find a use for kaolinitic clays, rejected from mining explorations, by thermal activation. At present, the mining exploration process is based on characterising the material in the mine, i.e. time is invested in drilling, obtaining and studying samples. These are then extracted and characterised, involving economic losses because not all the extracted and characterised material meets the specifications agreed with the clients that the sector supplies. The study shows that the thermal activation of these rejected kaolinitic clays widens the possible portfolio of products for mining sector companies. The feasibility of producing thermally activated kaolinitic clays was demonstrated on a laboratory scale, together with the innovation contribution for mining companies in enabling them to enter new markets by applying a technological variant such as clay calcination in their production process.

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