



Note

Ceramic behaviour of some clay deposits from Guayas province, Ecuador: Preliminary study



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ABSTRACT

This note is a preliminary study from mineralogical and chemical points of view about the possibility of using local clays from Ecuador in industrial ceramics. The chemical and mineralogical composition of clays was determined by X-ray fluorescence (XRF) and X-ray diffraction (XRD). Also, the plasticity index (PI) was measured for each sample. Test samples were prepared by pressing and firing at different temperatures. Linear contraction (LC), water absorption capacity (WAC), and bending strength were performed to characterise the fired clays. The clay deposits studied were plastic raw materials with very high contents of quartz. The raw material in traditional ceramics in Ecuador is clay with approximate levels of silica at 60%, alumina 15%, low alkalis and carbonates, and high iron levels. The sample mineralogy indicates quartz as a primary mineral, followed by plagioclases, with hematite to a lesser extent in all the samples. Kaolinite, illite, and chlorite are the main clay minerals in the raw material samples. All the studied clays seem to be easily adaptable to a correct dry pressing ceramic process. The studied clays are an excellent raw material for the formulation of low porosity ceramic stoneware.

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1. Introduction

In order to research the ceramic sector in Ecuador, certain basic information is necessary, such as the number of industries involved in the sector (Table 1), the raw material used (Table 2), and the products made (Cárdenas et al., 2003). Ceramic industries were also arranged by province, determining that the greatest percentage is based in the provinces of Azuay (37%) and Pichinga (21%). Guayas province (13%) is third overall, and the largest among Ecuador's coastal areas. Smaller producers include the provinces of Loja (10%), Chimborazo and Cañar (5%), Manabí, Tungurahua, and Imbabura (3%).

In Ecuador, only the traditional ceramic industry has been developed, and within this segment, the highest percentage corresponds to white and red ceramics (Cárdenas et al., 2003).

In order to determine which types of products the white and red ceramic industries manufacture, the industries were consulted directly. The results from this research indicate that the country produces roof tiles, clay bricks and blocks, stoneware tiles, floor and wall tiles, sanitary porcelain, and porcelain.

This study was focused on the properties of ceramic clays from Guayas province (Ecuador), an area with an important local traditional ceramic industry. Six deposits with industrial applications were studied. The clays come from Samborondon, Marcabeli, and San Roque Piñas, in Guayas province. The clays used for manufacturing traditional ceramic

handicrafts come from nearby savannas at depths of 25–30 cm. These clay deposits are Quaternary materials deposited during different episodes by the Guayas River.

The relationship between the mineralogical composition of the raw materials and phase changes taking place during their sintering under different conditions has been studied by different authors (Daskshama et al., 1992; Jordan et al., 1999, 2009, among others). A sintering process consists in the compaction of aggregated particles. This process is not complete so the ceramic tile bodies are still quite porous. Towards 1000 °C, the larger pores are seen to increase (between 1 and 10 μm). This phenomenon coincides with the destruction of clay minerals and their re-crystallisation (Jordan et al., 2008).

The raw material in traditional ceramics in Ecuador is clay with approximate levels of silica at 60%, alumina 15%, low alkalis and carbonates, and high iron levels (Cárdenas et al., 2003).

This study results from the necessity of the Ecuadorian ceramic industry to locate clays of high plasticity that additionally possess a high degree of cohesion upon drying and wide vitrification ranges; therefore, there is great interest in their ceramic behaviour.

Previous studies do not exist about these non-exploited clay deposits in Guayas province. This is the first time that the applicability of these clays as a raw material for the ceramic industry has been tested. New research and better characterisation of clay deposits were needed for obtaining new ceramic processes and formulations. The main objective of this paper was to study the chemical–mineralogical composition and technological behaviour that allows the evaluation of the applicability of the clay deposits studied in manufacturing new ceramic products.

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Table 1
Number and percentage of ceramic and related industries in Ecuador.

Industry	Number of companies	%
White clays	15	35
Red clays	15	35
Cement*	8	19
Glass	4	9
Refractory	1	2

* Limestone is used as a raw material in the ceramic and cement industries.

2. Materials and methods

Six deposits of clays were selected in the Samborondon (series EC-1, EC-2, EC-3, and EC-4), Marcabelli (series EC-5), and San Rafael Piñas (series EC-6), located in the Guayas province of Ecuador.

Twenty samples of each clay deposit were collected. Samples were taken according to standardised sampling procedures (Sanfeliu and Jordan, 2009). They were oven-dried at 110 °C until reaching a constant mass and then ground with a hammer mill to pass through a 630 µm sieve following normal ceramic laboratory practices (Meseguer et al., 2009a). Ten selected samples from each deposit were analysed for the mineralogical and chemical composition (average values are discussed). A representative sample of each deposit was selected for ceramic tests. Mixtures of samples from the same deposit were prepared in a proportion of 65% solid and 35% water with a 1% deflocculating agent (sodium pyrophosphate).

Mineralogical analysis was carried out by X-ray diffraction (XRD) using a Siemens D-5000 diffractometer, CuKα radiation, both on powder (bulk samples) and oriented aggregates (natural and reacted with ethylene glycol and heated to 550 °C for 2 h) of the clay fraction were obtained following the criteria expressed by Moore and Reynolds (1997). A semi-quantitative analysis was carried out following the Jordan et al. (1999) methodology. The chemical analysis was based on X-ray fluorescence measurements (Bruker S4 Pioneer) using conventional techniques (Meseguer et al., 2009b).

The plasticity index (PI) was determined with the Pfefferkon method (ten determinations per sample). Samples were moistened by hand, mixed sufficiently, and sieved (1 mm) until homogeneous agglomerates with 5% water were obtained. They were left to rest for 2 days and then pressed (0.3 MPa, 80 × 40 × 5 mm) using a laboratory press. The pieces were finally heated to 830, 880, 925, 980, 1025, 1080, 1120, and 1165 °C, maintaining at the maximum temperature for 2 h. These temperatures were arbitrarily chosen but correspond to temperatures used during the firing of industrial ceramic tiles. The linear contraction (LC) was measured following conventional techniques. The linear contraction is calculated as follows:

$$LC = \frac{L_i - L_f}{L_i} \cdot 100$$

where:

LC	linear contraction (%)
L_i	initial length of the ceramic body
L_f	final length of the ceramic body.

Table 2
Number of quarries for each raw material in Ecuador.

Raw material	Number of quarries
Limestone	24
Clays/kaolin	17
Silica	8
Gypsum	6

The water absorption capacity (WAC) was determined in fired clay pieces following the EN ISO-10545-3 (AENOR, 1997) standard. The bending strength tests were conducted at 1120 °C in a Gabbrielli Crab 424 instrument with a digital control system according to the EN ISO 10545-4 standard (AENOR, 2012). The temperature was selected following the standards for ceramic materials used for floor coverings. The values obtained show a high level of deviation, which made carrying out a high number of determinations (between 15 and 20) for each test necessary.

3. Results and discussion

3.1. Mineralogical composition

Some authors (Dondi et al., 1998; Jordan et al., 1999; Jordan et al., 2001; Dondi et al., 2014; among others) point out that mineralogical differences in raw materials have great influence on the behaviour of ceramic pastes with respect to their rheological and thermal properties, as well as the porous structure of the fired products.

The mineralogical compositions of the samples differed considerably (Table 3). Bulk samples from deposit EC-1 consisted mainly of quartz, plagioclase, and hematite, and contained illite in minor amounts. Quartz, illite/muscovite, and kaolinite were the dominant phases in clay fraction EC-1. Another component found in a lower quantity in this fraction was chlorite. Quartz and plagioclase were the dominant phases in bulk samples from deposit EC-2, while hematites, illite/muscovite, and chlorite were present in lower quantities. In clay fraction EC-2, the mineral phases found were quartz, illite/muscovite, and chlorite as the dominant phases, and the kaolinite content was minor. The main phases found in bulk EC-3 samples were quartz, plagioclase, chlorite, hematites, and kaolinite. The main phases in clay fraction EC-3 were kaolinite, quartz, and illite/muscovite. In this fraction, chlorite was found in trace amounts. The mineral composition of EC-4 samples in bulk rock consisted of quartz, plagioclase, kaolinite, chlorite, and hematites, with a small amount of illite/muscovite. In clay fraction EC-4, the mineral phases found were kaolinite and chlorite, with the dominant phases quartz and illite/muscovite. The mineral composition of EC-5 samples in bulk rock consisted of quartz, plagioclase, feldspars, and hematites, with a small amount of talc and illite/muscovite. In clay fraction EC-5, the mineral phases found were quartz as dominant phase, feldspar, illite/muscovite, kaolinite, and traces of chlorite. Finally, the mineral composition of EC-6 samples in bulk rock consisted of quartz, hematites, plagioclase, illite/muscovite, kaolinite, and talc. In clay fraction EC-6, the mineral phases found were quartz, the dominant phase, kaolinite, and illite/muscovite. Another component found in a lower content in this fraction was chlorite.

3.2. Chemical composition

The chemical composition (Table 4) of most samples showed a high iron content (7.3–5.1% Fe₂O₃), responsible for the reddish colour developing at firing, except for samples from the EC-5 deposit with a 0.6% Fe₂O₃ content. EC-5 C clays showed the highest relative amounts of alkalis (Na₂O + K₂O), explaining why this sample matures at relatively low temperatures. The CaO content was relatively low in samples EC-1, EC-2, EC-3, EC-4 (3.6–1.7%), and very low in samples EC-5 and EC-6 (0.1%). The CaO control is important because decarbonation is a strongly endothermic reaction that generates a high volume of gas, leading to expansive reactions (Cultrone et al., 2004). A higher loss on ignition was observed for the EC-2, EC-4, and EC-6 samples due to the presence of organic matter. Samples EC-1, EC-3, and EC-5 showed low values for ignition loss. Finally, the SiO₂ content was up to 60% in all studied samples, with Al₂O₃ values between 14 and 18%.

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