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Firing transformations of Chilean clays for the manufacture of ceramic tile bodies

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ABSTRACT

This contribution is focused on the study of the mineralogical changes occurring in the ceramic body after heating ceramic clays. Chile has an important local ceramic industry. Five deposits of clays with industrial applications were studied. The clays came from San Vicente de Tagua-Tagua (SVTT), Litueche (L), Las Compañías-Río Elqui (LC), La Herradura-Coquimbo (LH) and Monte Patria-Coquimbo (MP). The samples were heated to 830, 975, 1080 and 1160 °C keeping at the maximum temperature for 35 min. The bending strength of each ceramic body was determined at 1100 °C. Mineralogical analysis of the fired samples was carried out by X-ray diffraction. The SVTT contained quartz, spinel, cristobalite, microcline, albite, anorthite, hematite and enstatite; the LC clays quartz, mullite, spinel, microcline, albite, anorthite, hematite, diopside, enstatite, illite/muscovite and talc; the LH clays quartz, cristobalite, microcline, albite, anorthite, hematite, diopside, illite and augite; the MP clays quartz, cristobalite, microcline, albite, anorthite, hematite, diopside, gehlenite, enstatite and wollastonite and the L clays quartz, microcline and mullite. The persistence of illite at at least 900 °C was observed for LC and LH. SVTT and LH showed the required specifications for earthenware. The L clays were refractory clays with very low bending strength.

1. Introduction

During firing, a series of transformations occurs, which determine the final properties of the ceramic products (González-García et al., 1990; Jordán et al., 1999, 2001). During the ceramic process, once the crystalline structures of minerals exceed their stability limits, they are partially decomposed while simultaneously others are being formed. The destruction of the pre-existing structure does not occur instantaneously (Jordán et al., 1999). The knowledge of the origin, diagenesis and physicochemical composition of the clays is essential when sketching out suitable compositions required for ceramic production (Meseguer et al., 2009; Sanfeliu and Jordan, 2009). Upon firing, the minerals in the clay bodies undergo chemical and structural modifications deeply transforming the original clayey materials. The high temperature, low-pressure mineral transformations are mainly influenced by the chemical and mineralogical compositions of the original clay, its grain-size distribution, the maximum heating temperature, heating rate, duration of firing and kiln redox atmosphere (Maggeti, 1982; Moropoulou et al., 1995).

Firing in ceramic kilns was extensively reported in the literature. González-García et al. (1990) verified the presence of gehlenite and anorthite phases in fired clays which were originally composed of illite, kaolinite, quartz and calcite. Jordán et al. (1993, 1994, 1995, 1999) studied Cretaceous clays from Castellón, Spain and their behaviour when subjected to fast firing. Jordán et al. (2009) studied the firing transformations of non-calcareous Permo-Triassic clays used in the manufacture of ceramic tile bodies in the Spanish ceramic industry.

The relationship between the mineralogical composition of the raw materials and the phase changes during sintering was examined (Daskshama et al., 1992; Jordán et al., 1999, 2009). Between 900 and 1000 °C, the sintering process consists in the aggregation compacting of particles. As this process is not complete, the ceramic tile bodies are quite porous. The reduction of water absorption is linked to the increase in the bending strength of the clay matrix and the thermal expansion of the ceramic piece increases.

Above 1000 °C for some samples and above 1050 °C for other samples, high levels of sintering are reached, indicated by the fast decrease of water absorption. Towards 1000 °C, the larger pores increase (between 1 and 10 μm). This phenomenon coincides with the destruction of illites, chlorites and their re-crystallisation into quartz and spinel (Jordán et al., 2008). Several authors checked that the porosity of ceramic pieces is an important factor in their resistance to freezing temperatures (Wagh et al., 1993). The mechanical properties of ceramic pieces are very important in determining their application for any specific function (Boccaccini, 1994; Zweben, 1991). Also, the porosity of a ceramic body is related to its bending strength.

Wagh et al. (1993) proposed relations between bending strength and porosity in polycrystalline ceramic materials. The equations proposed for the model were reported by Jordán et al. (2008). The applicability of this model is limited to the availability of experimental

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data and has no predictive character. For this reason, only qualitative relationships among bending strength, porosity and mineral phases present in the ceramic bodies were obtained by Maiya et al. (1993). Ceramic clays are one of the most complicated ceramic systems because of the very complex relationship between the behaviour of minerals during the ceramic processing and the transformations during heating. A major challenge is to predict the phase transformations in silicate ceramics, since complex relationships occur between the structural characteristics of the fired products and the physical properties. Clay minerals undergo a complex path of thermal transformations during heating.

The focus of this study, therefore, was the analysis of the mineralogical changes of the ceramic bodies after heating industrial clays from Chile, and to evaluate the firing transformations in terms of crystalline phases.

2. Materials and methods

Five deposits of Chilean clays which can be used in the formulation of ceramic pastes were selected. The clays came from San Vicente de Tagua-Tagua (SVTT), Litueche (L) in the VI Region of Chile, and Las Compañías-Río Elqui (LC), La Herradura-Coquimbo (LH) and Monte Patria-Coquimbo (MP) from the IV Region of Chile. The geological background of the mineralogical and chemical compositions of these clays was described by Meseguer et al. (2010).

The clays are kaolinic–illitic clays with a high quartz content. Chlorite can also be present. Thermodilatometric analysis and the relationship between linear contraction and water absorption were discussed by Meseguer et al. (2010).

Eight samples of each clay deposit were collected. They were oven-dried at 110 °C until constant mass and then ground with a hammer mill to null residue in the 630 μm control sieve, following the normal practice in ceramic laboratories. A representative sample of each deposit was selected for firing tests.

To simulate industrial pressing conditions, the clays were moistened by hand, mixed and sieved (<1 mm) until homogeneous materials with 6% water were obtained. They were left to rest for 24 h and then pressed (0.3 MPa, 80×40×5 mm) by a laboratory press. The pieces were heated to 830, 975, 1080 and 1160 °C, keeping at the maximum temperature for 35 min. Analysis of the fired samples was carried out by X-ray diffraction (XRD) using the Siemens D-5000 diffractometer, CuKα radiation.

The bending strength of fired bodies was measured at 1100 °C following standard methods with the Grabbrielli Crap 424 with a digital control system.

3. Results and discussion

3.1. Mineralogical composition of the fired samples

The mineralogical transformations are reported in Tables 1 to 5. The XRD reflection at 10 Å corresponded to dehydroxilated mica (illite/muscovite). The reflection of sample LC was reduced with increasing firing temperature above 830 °C and disappeared at 975 °C (Table 2). The persistence of illite was observed up to at least 975 °C for LH (Table 3). Spinel was formed in the SVTT and LC series (Tables 1 and 2). Diopside in the MP series formed, probably from decomposition of the Mg rich chlorite (Table 4). Enstatite appeared at 830 °C in the series LC (Table 2) and at 1080 °C in the SVTT series (Table 1), and was stable up to the temperature of 1160 °C. Thus enstatite is preferably formed in samples with higher chlorite contents. Anorthite was formed at 830 °C and reached the maximum amount at 1160 °C in the LC, LH and MP series (Tables 2–4). In the SVTT series (Table 1), anorthite appeared at 830–980 °C but disappeared at higher temperatures. Wollastonite was present in the MP series (Table 4). Usually, wollastonite and gehlenite are considered intermediate compounds which become unstable in the presence of SiO_2, forming anorthite (Jordán et al., 2001; Trindade et al., 2009). Quartz decomposed between 830 and 1180 °C. The decomposed and disappearing phases contribute to the formation of a vitreous phase, up to 830 °C. Besides hematite formation, new crystalline phases appeared. At 1160 °C mullite was formed in the series LC (Table 2).

Table 1
Mineralogical transformations of SVTT clays during heating at 830–975–1080–1160 °C.

Mineral phase	SVTT 830 °C	SVTT 980 °C	SVTT 1080 °C	SVTT 1160 °C
Quartz	++++	++++	+++	+++
Spinel	(+)	(+)	(+)	(+)
Cristobalite	(+)	(+)	++	++
Microcline	+++	++	+	−
Albite	++++	++	−	−
Anorthite	+	+	−	−
Hematite	+	+	++	++
Enstatite	−	−	+	+

Legend: ++++ (>20%); +++ (>15%); ++ (>10%); + (>5%); (+) present (<5%); and − not present.

Table 2
Mineralogical transformations of LC clays during heating at 830–975–1080–1160 °C.

Mineral phase	LC 830 °C	LC 975 °C	LC 1080 °C	LC 1160 °C
Quartz	+++	+++	+++	++
Mullite	−	(+)	(+)	(+)
Spinel	−	−	+	++
Microcline	+	+	(+)	(+)
Albite	++++	++++	+++	++
Anorthite	++	+++	+++	++++
Hematite	+	+	+	+
Diopside	−	−	−	(+)
Enstatite	(+)	+	+	+
Illite/muscovite	(+)	−	−	−
Talc	(+)	(+)	−	−

Legend: ++++ (>20%); +++ (>15%); ++ (>10%); + (>5%); (+) present (<5%); and − not present.

Table 3
Mineralogical transformations of LH clays during heating at 830–975–1080–1160 °C.

Mineral phase	LH 830 °C	LH 975 °C	LH 1080 °C	LH 1160 °C
Quartz	++++	++++	+++	+++
Cristobalite	−	−	(+)	+
Microcline	++	++	+	+
Albite	+++	++	−	−
Anorthite	+	++	+++	++++
Hematite	+	+	+	+
Diopside	+	+	+	(+)
Augite	−	−	(+)	(+)
Illite	+	(+)	−	−

Legend: ++++ (>20%); +++ (>15%); ++ (>10%); + (>5%); (+) present (<5%); and − not present.

Table 4
Mineralogical transformations of MP clays during heating at 830–975–1080–1160 °C.

Mineral phase	MP 830 °C	MP 975 °C	MP 1080 °C	MP 1160 °C
Quartz	+++	+++	+++	++
Cristobalite	−	−	−	++
Microcline	+	+	+	+
Albite	++++	+++	−	−
Anorthite	++	+++	++++	++++
Hematite	++	++	++	++
Diopside	(+)	(+)	+	+
Gehlenite	(+)	(+)	(+)	(+)
Enstatite	(+)	(+)	+	++
Wollastonite	(+)	(+)	(+)	(+)

Legend: ++++ (>20%); +++ (>15%); ++ (>10%); + (>5%); (+) present (<5%); and − not present.