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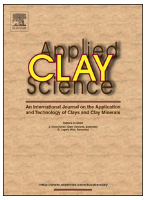

Research Paper

High temperature phase evolution of Bolivian kaolinitic–illitic clays heated to 1250 °C

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ABSTRACT

The thermal behaviour of two types of clays collected from different locations in Bolivia has been studied. The clays contain kaolinite, illite, quartz and small amounts of microcline. The phase evolutions have been characterized from room temperature to 1250 °C. For both clays, kaolinite is completely transformed into metakaolinite when heated up to 650 °C. During further heating to 1050 °C, illite undergoes total dehydroxylation. Mullite is formed in the temperature interval of 1050–1150 °C and its formation rate is dependent on the amount of K and Fe present in the clays. The clay with higher amounts of K (3.2 mass %) and Fe (5.6 mass%) has an onset temperature for sintering at about 900 °C and an onset temperature for liquid formation at 1080 °C. This is about 50 °C lower onset temperature for sintering and 94 °C lower onset temperature for liquid formation when compared with the clay with lower amounts of K (2.3 mass %) and Fe (1.6 mass %).

1. Introduction

The prospect of using clays as building materials is attractive for undeveloped countries as it may lead to the development of new domestic industries when adding value to natural resources. Clay deposits are considered as a complex mixture of several different types of minerals. They can contain quartz, feldspars, micas, smectites, chlorites, and others, with exchangeable ions such as iron- alkaline- and alkaline earth- ions located either in the interlayers or in the internal structures of the clay minerals (Bétard et al., 2009; Prudêncio et al., 2002).

Clay materials from tropical regions of Bolivia, located in the eastern lowlands including large sections of Amazonian rainforest and the Chaco plain, have traditionally been used to manufacture building materials. Building ceramic involve products such as roof-, floor- and wall tiles and bricks. There are some required properties of clays to be suitable for such products. The most important properties of building ceramic are high strength and low porosity. According to technical standards (BS 6073, 1981) bricks with compressive strength values higher than 10 MPa are classified as solid bricks with good quality, and the porosity could vary but is usually above 10 vol.%.

Alkaline and alkaline earth ions are known as fluxing components and can promote the formation of a liquid phase at lower temperatures during firing, which will increase the rate of densification and improve the final strength (Das and Dana, 2003; Milheiro et al., 2005).

Aesthetic aspects such as the colour of the final product are also important. For example, a red or red-brown ceramic can be achieved if the raw material contains Fe, which can be transformed into hematite (Fe_2O_3) during firing under oxidizing conditions (Stepkowska and Jefferis, 1992).

Knowledge of the quality and characteristics of the raw material is a main aspect prior to any clay-based process. In this context many studies have been conducted to ascertain the quality of different clay based materials in other countries with a large tile and brick production and a high technical standard, such as Italy, Spain, Brazil, and India (Bauluz et al., 2003; Dondi et al., 2001; Manoharan et al., 2011; Vieira et al., 2008). However, few studies have been carried out on clays from Bolivia and the lack of more knowledge of the characteristics and properties of these clays has led the local ceramic factories to exploit the clay deposits empirically. In particular, illite–kaolinite-rich clays have shown appropriate properties for building ceramic (Aras, 2004; González-García et al., 1990). Thus, the suitability of different clays in different applications is strongly dependent on its mineralogical and chemical composition (Gualtieri et al., 2010; Mandour et al., 1989).

On the other hand, alkaline, alkaline earth ions and iron affect the thermal behaviour and phase formation during heat treatment and consequently influence the final mechanical properties of the building ceramic (Alizadeh et al., 2004; Mota et al., 2008; Schmidt-Reinholz and Schmidt, 1995). Therefore, the chemical and mineralogical composition, the thermal behaviour and possible phase formations need to be

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considered in detail before suitable clay qualities can be selected for building applications.

The aim of this work was to characterize and study the evolution, phase formation and microstructural changes during heating of two different natural clays from Bolivia, via a combination of several techniques such as DSC/TG, dilatometer, XRD and SEM, in order to determine the suitability of these clays as raw material for building applications.

2. Materials and methods

The Chapare region hosts the largest deposits of clays found in Bolivia. The clay areas are several hundred square kilometres. The clay deposits located at the small hills around the Ivirgarzama area are denoted IC clay, and the deposits found on the soils of the Entre Rios zone and its surrounding areas are denoted EC clay. Ivirgarzama and Entre Rios are located 220 and 265 km east from the city of Cochabamba. The coordinates and locations within Bolivia of the two main deposits are shown in Supplementary Fig. 1.

In order to ensure representative samples, the clays were collected from several different parts of each deposit. The samples coming from the same deposit were mixed, sun-dried and then quartered into small fractions of about 5 kg. The small fractions were dried at 110 °C and then ground to a fine powder in an agate mortar until all powder passed through a 315 μm size sieve. The ground and sieved powder was used as representative samples for all experiments.

2.1. Characterization of collected representative clay samples

The material was characterized by X-ray powder diffraction (XRD). The X-ray diffractograms were obtained with a Siemens D 5000 X-ray diffractometer with CuKα radiation ($\lambda = 1.5418$ Å). X-ray diffractograms were recorded in the 2θ range between 5° and 50° with a step size of 0.02°. The phases were identified from peak positions and intensities using reference data from the ICDD (2010). Chemical analyses of the collected clays were performed by a certified analytic laboratory (ALS Scandinavia, Sweden) by inductively coupled plasma with atomic emission spectroscopy (ICP-AES).

2.2. Thermal analysis

Differential scanning calorimetry and thermogravimetry (DSC/TG) were performed to investigate the phase evolutions and mass changes during heating. The experiments were performed in a Netzsch STA 449C Jupiter instrument, equipped with a Netzsch Aeolos QMS 403C mass spectrometer. The DSC/TG experiments were carried out on powder samples in an alumina crucible between room temperature and 1300 °C at a heating rate of 10 °C/min in air atmosphere.

The dilatometry experiments were performed in a Netzsch DIL 402C instrument. Prior to measurement, the compacted sample was dried overnight at 110 °C. The samples were heated from room temperature to 1150 °C in air atmosphere at a heating rate of 10 °C/min. The density and open porosity of the samples were determined using Archimedes' principle.

2.3. Characterization of heat treated material

The clays were heat treated in a chamber furnace in air atmosphere at the following test temperatures: 450, 650, 950, 1050, 1150 and 1250 °C. The heating rate was 10 °C/min up to the final temperature, and then the samples were furnace-cooled. The selected temperatures were chosen based on the results from the thermal analysis. The phase identification of the sintered specimens was performed by X-ray diffraction as described above. The morphology of the collected clays and the samples heat treated to 1150 °C and 1250 °C (before and after chemical etching for 10 min in HF acid with a concentration of 11 mol/L) was studied by scanning electron microscopy (SEM) using a Jeol 6460-LV microscope.

3. Results and discussions

3.1. Characterization of collected clay samples

X-ray diffractograms from the two materials (IC and EC) are shown in Fig. 2. All peaks in the diffractograms above the background were identified. See also comments below, where the positions of the three strongest peaks of each phase are also given.

The main clay minerals identified in both samples are kaolinite and illite. The EC sample also contains smectites. The major non-plastic component present in the clays is quartz and small amounts of microcline are also detected in both samples.

Rational mineralogical composition analysis is shown in Table 1a. The relative quartz content in the IC clay was estimated to be about twice as high compared with the EC clay. The presence of quartz in clays has been suggested to enhance the workability, diminish shrinkage and reduce the risk of crack formation during drying. Moreover, quartz phase in the clays has proven to be important to increase both strength and toughness in some ceramic based materials (Steinbrech, 1992). Vieira et al. (2008) concluded that an addition of quartz was necessary to improve workability of some clays from Rio de Janeiro (Brazil), especially for brick fabrication. Likewise, some clay from Burkina Faso needed an extra addition of quartz sand, feldspar and talc to obtain

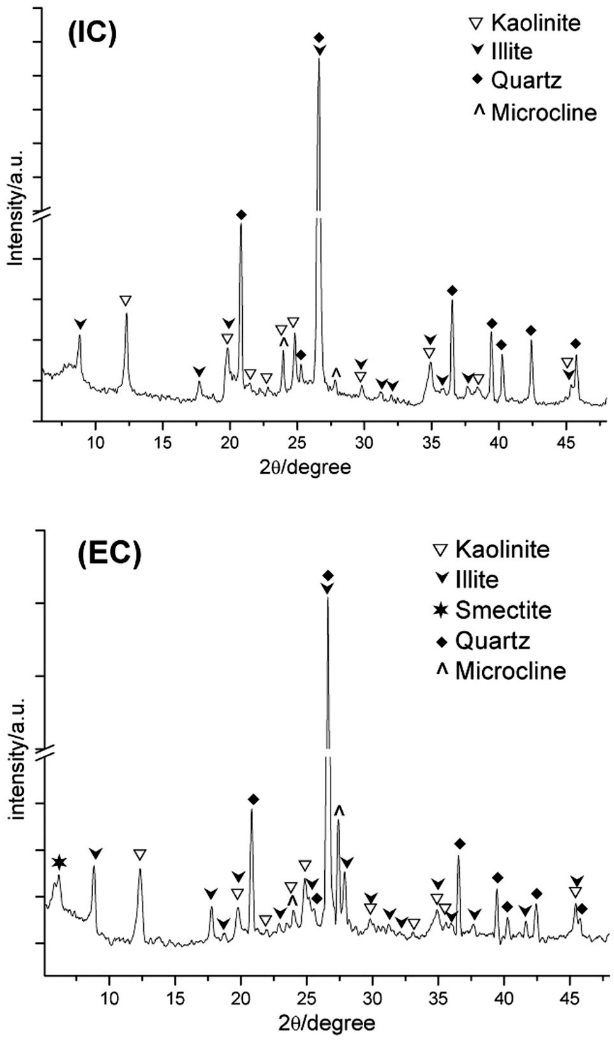

Fig. 2. X-ray powder diffractograms of collected IC and EC clays.

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