Research paper

Mineral and textural transformations in aluminium-rich clays during ceramic firing

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ABSTRACT

The aim of this study has been to analyse the mineralogical and textural transformations of a set of aluminium-rich shales of interest for refractory and ceramic uses, fired from 800 °C to 1300 °C. To that end, raw and fired samples were analysed by X-ray diffraction, transmitted light microscopy, field emission scanning electron microscopy, and transmission electron microscopy. Raw samples comprise variable proportions of illite, pyrophyllite, orthoclase, quartz, kaolinite, mixed-layer I-Sm, and organic matter. At temperatures below 800 °C, kaolinite, mixed-layer I-Sm, and organic matter are destabilized, indicating that they are the least stable phases in the firing process. Illite, pyrophyllite, and orthoclase remain until 1000 °C and show a broader stability field during firing than in natural environments. Quartz persists throughout the entire firing process, although it is partly replaced by vitreous phase. Hematite crystallizes at 900 °C. Vitrification begins at 1000 °C, marking the first significant textural change. From 1000 °C mullite starts to crystallize from the Si- and Al-rich vitreous phase. The mullite composition is not stoichiometric and probably as temperature increases Si is partially replaced by Al, Fe and Ti in the structure. Nevertheless, with the increase of the firing temperature, the mullite composition is closer to the theoretical composition and also to that of natural mullites. Furthermore its crystal thickness increases with temperature up to 70 nm.

1. Introduction

Nowadays, aluminium-rich clays with kaolinite and pyrophyllite are of great industrial interest because these clays are the most important raw material in stoneware and high-quality ceramic floor tile manufacturing as well as in refractory ceramics. Due to this interest, knowledge of the phases and mineral transformations taking place during firing is useful in order to determine the most appropriate conditions for the dynamic of the firing and vitrification temperatures. In order to understand the ceramic process it is important to deepen in the knowledge of textural changes, mineral reactions and variations in compositions of the phases with the increase of the temperature both at micron and nano scale.

Previous papers (Cultrone et al., 2001; Wattanasiriwech et al., 2009) have described mineralogical and textural changes in illite and smectite rich-clays with variable proportions of carbonates during firing. In general, these works show an increase of the vitrification process and crystallization of new phases as mullite, and/or Ca, Mg silicates with temperature. As Maggetti (1982) indicates, the mineral transformations that occur when a clay-rich sediment is fired in a process with high-T and low-P are mainly influenced by the

mineralogical composition of the raw clay-rich material, its granulometry, the firing temperature as well as the kiln atmosphere conditions.

To conduct the study, a set of aluminium-rich shale samples from the Iberian Range (in NE Spain) were selected. Samples from this location had been previously studied by Bauluz and Subías (2010) in order to determine their mineral composition and genesis. These shales are characterized by significant amounts of pyrophyllite and kaolinite, organic matter, and the absence of carbonates. The shale mineralogy consists of quartz, pyrophyllite, illite, micas, mixed-layer illite/smectite (I-Sm), chlorite, and kaolinite (Bauluz and Subías, 2010).

The aim of this work was to combine X-ray diffraction (XRD), optical and field emission scanning electron microscopy (FESEM), and transmission electron microscopy (TEM) in order to describe and determine the mineralogical and textural changes of residual and newly formed phases in samples fired at different temperatures. The chemistry of transformed and/or neoformed phases was also given particular consideration.

2. Geological setting

The samples analysed in this study were taken from a shale outcrop

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in the western branch of the Iberian Range at the following geographical coordinates: N40°35′24.7″ W01°46′49.0″ elevation 1365 m (sample BSCH-7B), N40°28′26.2″ W01°38′47.1″ elevation 1571 m (sample CHECA-3B), and N40°27′44.2″ W01°37′58.1″ elevation 1447 m (sample CHECA-5B). Samples belong to the Pizarras de Checa Formation, Upper Aeronian to Lower Ludfordian (Gutiérrez-Marco and Storch, 1998). The coexistence of pyrophyllite, mixed-layer I-Sm, illite, kaolinite, and chlorite is due to the combination of sedimentary, low-grade metamorphic- and low-temperature hydrothermal processes (Bauluz and Subías, 2010). According to these authors, three stages are identified: 1) Black shale deposition and subsequent diagenetic processes that produced the coexistence of quartz, illite, kaolinite, and organic matter. 2) Intrusion of andesite sills producing hydrothermal alteration and the crystallization of pyrophyllite, illite, mixed-layer I-Sm, and jarosite. 3) Shales, sill folding, and penetrative foliation leading to the recrystallization of illite and paragonite.

3. Materials and methods

3.1. Samples and firing process

The selection of the samples for this study, labelled as CHECA-3B, CHECA-5B, and BSCH-7B, was made on the basis of their mineralogy. The three samples contain pyrophyllite, kaolinite and illite in different proportions. Therefore they are appropriate to analyse de mineralogical changes of these clays with firing.

Cylinders (4.5 cm in diameter and 2.5 cm high) were manufactured from the raw clays by pressing the under 400 μm fraction of the milled samples and then fired in a Tecno-piro PR4T oven. The firing temperatures were 800 °C, 900 °C, 1000 °C, 1100 °C, 1200 °C, and 1300 °C under oxidizing conditions, with temperature steps of 200 °C/h, and the maximum temperature maintained for 2 h.

3.2. X-ray diffraction

Mineralogical analyses were performed by X-ray diffraction (XRD) on the three natural samples and those fired at different temperatures. To obtain the diffraction patterns, a Philips 1710 diffractometer was used with 40 kV voltage, 30 mA current, CuKα, automatic slit, and a graphite monochromator. XRD patterns were obtained from the 3–80°2θ interval with a goniometer velocity of 0.03°2θ/s and an integration time of 0.5 s. The record was made with the Software XPowder (Martín, 2007).

Once the minerals present in the samples were determined, the values of the reference intensity ratios (RIR) of each mineral phase were established, with corundum (cor). The RIR value is the relation between the intensity of the peak of interest and that of the standard peak in an XRD pattern. This value allows us to subsequently quantify the different minerals in the samples. To obtain the RIR value, pure standards were selected for hematite (NENO90 from Tierga, Spain), illite (Source Clays Repository from Silver Hill, Mont), kaolinite (Source Clays Repository from Warren County, Georgia, USA), mullite (HKT, France), orthoclase (Bancroft, Canada), pyrophyllite (Pyshminskoe deposit from Berezovskii, Rusia), and quartz (Barrueco Pardo, Salamanca, Spain) in order to compare them with the proportions of these minerals in our samples. It was not possible to get a standard for mixed-layer I-Sm.

Following the procedure described by Hillier (2003), various mixtures were prepared of the standards with corundum in known concentrations. These mixtures were then studied by XRD, and the pattern obtained in this case has a 3–50°2θ interval with a goniometer velocity of 0.1°2θ/s and an integration time of 0.4 s. Knowing the percentage of corundum and standard in each mixture and the characteristic reflections of each phase in the XRD patterns, the RIRcor of each standard was calculated using an x-y graph. This graph (Fig. 1) shows the relation of the standard percentage with respect to the corundum (abscissa) versus the relation of the standard characteristic reflection intensity

with respect to the corundum reflection (ordinates).

After determining the RIRcor for each standard, natural and fired samples were mixed with 10% corundum and analysed by XRD in order to quantify the weight percent (%wt) of each mineral present. Working conditions in the diffractometer were the same as those used for the standards. The amount (X) at each stage (i) in a mixed sample with corundum can be obtained with the formula: $X_i = [X_{cor}/RIR_{cor}][I(hkl)_i/I(113)_{cor}]$.

X_{cor} is the percentage of corundum mixed with the test sample, RIR_{cor} the reflective power of each standard with respect to corundum, $I(hkl)$ is the absolute intensity of the characteristic reflection of each mineral phase, and $I(113)_{cor}$ is the intensity of the (113) peak (2.08 Å) of corundum. The results must be divided by 0.9 to obtain percentages (%). The content of non-detected phases by XRD (e.g. amorphous or poor crystalline phases) and non-quantified phases (e.g. mixed-layer I-Sm) is obtained by default to add up to 100 ("Others" in Fig. 2). Reflections (hkl) used to determine the RIRcor of each mineral were 2.69 Å for hematite, 10 Å for illite, 7.17 Å for kaolinite, 3.38 Å for mullite, 3.24 Å for orthoclase, 9.2 Å for pyrophyllite, and 3.34 Å for quartz.

3.3. Optical and electron microscopy studies

As the XRD results show the mineralogical changes were very similar in all three samples, sample CHECA-3B was chosen at random for the microscopy studies. First, thin sections of this sample (fired at different temperatures) were studied by transmitted light microscopy to identify the mineralogy and characterize its texture.

XRD results and transmitted light microscopy observations show that the sample fired at 900 °C had a similar texture and mineralogy to that fired at 800 °C. Therefore, samples fired at 800, 1000, 1100, 1200, and 1300 °C were selected for study by electron microscopy. Thin sections of those samples were analysed by a Carl Zeiss Merlin field emission scanning electron microscope (FESEM) with an Oxford energy-dispersive X-ray (EDS) detector at the University of Zaragoza (Spain). Thin sections were previously coated with carbon.

Compositional images of the sample were obtained using two types of backscattered electron detectors: angular selective backscattered (AsB) and energy selective backscattered (EsB). To obtain chemical information, semi-quantitative analyses were acquired by energy-dispersive X-ray (EDS). This latter technique has a detection limit of 0.1%. The accelerating voltage for AsB and EDS was 15 kV with a beam current of 400 pA; for EsB, the accelerating voltage was 4 kV with a beam current of 2.0 nA.

In order to establish the presence of a vitreous phase and its composition and relation with other mineral phases as mullite, sample CHECA-3B fired at 1000 °C, 1100 °C, and 1300 °C was analysed by Electron Microscope (TEM). The study was performed using a Jeol-2000 FXII TEM equipped with an Oxford energy dispersive spectroscope (EDS) at the University of Zaragoza. The accelerating voltage was 200 kV with a beam current of 20 mA. For this study, a thin section (20 μ thick) was prepared and attached to the glass with Canada balsam, which melts on contact with heat. Copper rings (3 mm in external diameter and 1 mm in internal diameter) were attached in representative areas of the samples. Subsequently, the rings were cut off and ion milled with an ionic ION DUO MILL GATAN thinner, making them electron transparent.

4. Results

4.1. X-ray diffraction (XRD)

4.1.1. RIRcor calculation

The qualitative XRD study indicates that samples are formed by mixed-layer I-Sm, kaolinite, illite, pyrophyllite, hematite, mullite, quartz, and orthoclase.