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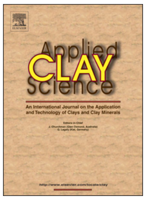

Research paper

Mineralogical composition and particle size distribution as a key to understand the technological properties of Ukrainian ball clays

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ABSTRACT

The ball clays from the Donetzk basin, Ukraine are widely utilized in the production of ceramic tiles. Their commercial success stems from unrivaled technological properties, whose link to mineralogical composition and particle size is not well understood yet. This work is an in-depth investigation of the mineralogical, chemical, and physical properties with the aim to disclose the reasons of the peculiar technological behavior of these clays. Five clay samples were studied by XRF, XRD (bulk and fractions <2 μm and <0.2 μm), SEM, TEM, rheological characterization, particle size distribution, BET, MBI, Pfefferkorn index, Atterberg plasticity limits, and laboratory simulation of the tilemaking process. The Ukrainian clays are very fine-grained and characterized by poorly ordered kaolinite (Kaol), interstratified illite/smectite (I–Sm) and a low quartz content. The Kaol-to-I–Sm ratio is lower than in conventional ball clays and two different I–Sm types are found to be predominant in the colloidal fraction. Morphologically, clay minerals appear to be mostly subhedral lamellae that curl and fold under pressure. These characteristics explain the outstanding technological properties of Ukrainian clays and particularly their high plasticity and suitable rheological behavior. These properties depend on the peculiar conjunction of mineralogical and grain size factors that are difficult to be reproduced by clay blending or mixing design.

1. Introduction

Ball clays have been increasingly utilized in the ceramic production to the point that the tilemaking industry turned to be the major end user, in particular in porcelain stoneware tiles (Sánchez et al., 2010; Dondi et al., 2014). Ball clay is defined as "*fine-grained, highly plastic, mainly kaolinitic clay, the higher grades of which fire to a near white color in oxidizing atmosphere*" (Wilson, 1998; Bergaya and Lagaly, 2013). The picture of compositional and technological properties of this kind of clays was well established (Worrall, 1975; Powell, 1996; Harvey and Murray, 1997; Wilson, 1998) by the time when the Ukrainian clays were for the first time exported at the end of 1992 (Fiederling-Kapteinat et al., 2000). These clays come from the Donetzk basin (Donbas) where fluvio-lacustrine Miocene sedimentary deposits are exploited (McCuistion and Wilson, 2006; Murray, 2006a; Mariani, 2010). Ukrainian clays rapidly gained two thirds of the international market, attaining a yearly output of around 2 million tons and an overall export of over 30 million tons up to date (Fiederling-Kapteinat, 2004; Bal and Fiederling-Kapteinat, 2007; Mariani, 2010). The reasons of such a commercial success stem from the unrivaled technological features that Ukrainian clays exhibit: suitable rheological properties, high plasticity, proper behavior during compaction and drying, and easy sinterability (Dondi et al., 2003; Galos, 2011a,b). Along with a worldwide acceptation as a premium product (Fiederling-Kapteinat, 2004, 2005; Zanelli et al., 2011), these characteristics render Ukrainian clays very useful in the ceramic tile production to turn easier some manufacturing steps (less defects and higher rate of prime quality products) and to produce large ceramic slabs, e.g. 360 cm × 120 cm × 0.3 cm (Raimondo et al., 2010; Sánchez et al., 2010). Furthermore, they enable the recourse to low-priced raw materials, whose non-optimal features may be balanced by the better performances of the Ukrainian clays (Galos, 2011a,b; Zanelli et al., 2011). The same targets are harder to be achieved utilizing conventional ball clays of lower performance (Lombardo, 1996).

The causes of the outstanding properties of the Ukrainian ball clays are not fully understood yet. Although there are evidences of the role played by particle size distribution and "crystallinity" of clay minerals (Dondi et al., 2003; Galos, 2011a,b; Petrick et al., 2011), a comprehensive evaluation is still lacking.

The purpose of this work is an in-depth investigation of the mineralogical, chemical, and physical properties of Ukrainian clays in order to disclose the variables that control their peculiar technological behavior, comparing their performance with those of conventional ball clays,

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including smectite-bearing samples. The results will provide a key to improve the technological response of common ball clays exploited all over the world.

2. Experimental

Five clay samples (named UA, UB, UD, UK, US) were obtained by suppliers of Ukrainian raw materials. The sample selection was carried out in order to cover the spectrum of mineralogical and technological features of commercial clays, as inherited by differences between the main quarries in the Donetzk basin (Fiederling-Kapteinat, 2005; Mariani, 2010). The features of conventional ball clays were taken from the literature (Dondi et al., 2014 and references therein).

The mineralogical composition was investigated by X-ray powder diffraction performed on both randomly oriented specimens (bulk) and on oriented specimens of the <2 μm and <0.2 μm fractions (air dried and saturated with ethylene glycol). The fine fractions were extracted by sedimentation, according to Stokes' law, and centrifugation (Moore and Reynolds, 1997). A Rigaku-Denki Geigerflex Max III C diffractometer ($0.5°2\theta\ \mathrm{min}^{-1}$, graphite-monochromated CuKα radiation) was used. Kaolinite structural order was estimated according to the Hinckley's and Stoch's methods (Aparicio and Galan, 1999) and the AGF index (Aparicio et al., 2006). The interpretation of XRD patterns was performed according to Moore and Reynolds (1997) and Środoń (2006). A quantitative composition of the bulk samples was calculated following Domínguez et al. (2008). Composition of the fine fractions was estimated by diffraction peak deconvolution, taking into account the area of the 001 reflection of kaolinite (Kaol) and interstratified illite/smectite (I–Sm).

The microstructure was observed by both scanning electron microscopy (SEM, JEOL 35 CF) and transmission electron microscopy (TEM, JEOL 100 CX). Small clay fragments, mounted on copper holders and coated with Au–Pd alloy, were used for SEM observations. Clay–water dispersions were sprayed on 200 mesh copper holders and bright field technique was used for TEM observations. In addition, the texture of the rods (in section) used to determine the Atterberg plastic limit was observed under SEM.

Whole rock chemical analysis of major elements was performed by wavelength-dispersive X-ray fluorescence spectrometry (XRF-WDS) on powder pellet pressed with micronized wax.

Particle size distribution was measured by X-ray monitoring of gravity sedimentation (Micromeritics Sedigraph 5100, ASTM C 958) and wet sieving of the >100 μm fraction (ASTM C 325). Specific surface area (SSA) was determined by nitrogen absorption using the BET method (Micromeritics FlowSorb II, ASTM C 1069).

Rheological properties were measured by a stress-controlled rotational rheometer (Bohlin CVOR 120, Malvern, UK) equipped with coaxial cylinders (C25: outer diameter 27.5 mm, gap 1.25 mm). The temperature was kept at 30 °C with a thermal control unit based on water jacket. The same protocol of measure was applied to all the samples (Fig. 1). It was made of three main parts: the first one was an on–off procedure in order to study the effect of the rest time on the rebuilding of the dispersions; the second part was a sequence of steps with a decreasing shear rate in order to get steady flow curves; and the last one was a triangular procedure to obtain an indication on thixotropy (Gardini and Galassi, 2010).

For the rheological measurements, 50% of mass aqueous dispersions of Ukrainian ball clay in deionized water, in the presence of 0.3% mass of sodium polyphosphate (supplied by Riedel-deHaën) with respect to the dry powder, were prepared. The dispersions were gently ball milled for 16 h to disagglomerate the particles.

Plasticity was assessed by measuring Atterberg consistency limits (ASTM D 4318), Pfefferkorn plastic index and the methylene blue index (MBI, Chiappone et al., 2004, pH ~4, ASTM C 837).

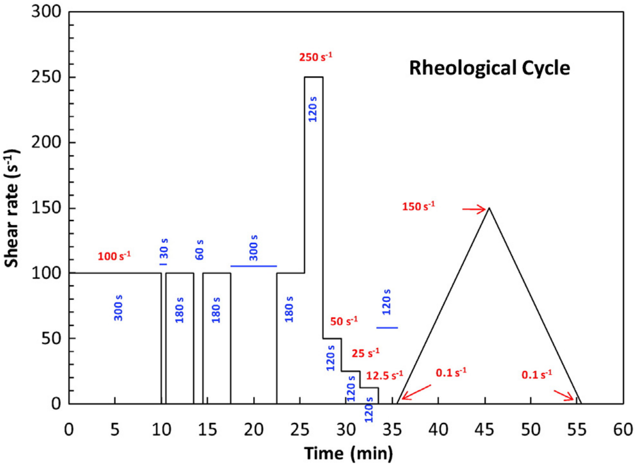

Fig. 1. Rheological protocol applied to the five samples of Ukrainian ball clays.

A laboratory simulation of the tilemaking processing was carried out (Dondi, 2003) by wet ball milling (planetary mill); slip drying (105 °C overnight in oven); powder agglomeration (8% mass moisture); uniaxial pressing (40 MPa) of 10 cm × 5 cm × 0.5 cm tiles; drying in an oven (105 °C overnight); fast firing in roller kiln (1200 °C, 60 min cold-to-cold). The following technological properties were determined: green bulk density (mass/volume); post-pressing expansion, powder compressibility and drying shrinkage (Dondi et al., 2008); green and dry modulus of rupture, firing shrinkage, water absorption and bulk density (Murray, 2006b).

3. Results and discussion

3.1. Technological properties

The behavior of Ukrainian clays during the tilemaking process can be compared with those of conventional ball clays by considering the key parameters governing the milling, pressing, drying and firing stages. The ball clays used in ceramic tile manufacturing show a wide range of technological properties (Dondi et al., 2014) as outlined by the rather large standard deviations (Table 1). The behavior during body preparation (ball milling to spray drying) will be considered at the next paragraph by discussing the rheological properties.

Ukrainian clays exhibit low values of expansion after pressing, stemming from poor elastic release once the load is removed. This plastic behavior eases pressing of large size and/or thin slabs by preventing breakage during decompression and tile removal from the mold. Thanks to the special properties of highly plastic clays difficult rectangular shapes and even tiles as big as 360 cm × 120 cm and just 3 mm thick are currently manufactured (Raimondo et al., 2010).

Comparing the compaction behavior for analogous moisture content, Ukrainian clays present a lower compressibility than conventional ball clays, besides the latter exhibit a lower degree of plasticity. This circumstance is to a large extent a consequence of the particle size distribution, since fine-grained materials are harder to be compacted. In this case, the different compressibility is not detrimental, as the dry bulk density is practically the same or even better than conventional ball clays. This is technologically important: the denser are the unfired tiles, the lower is their firing shrinkage, for a given water absorption.

The mechanical strength of both green and dry Ukrainian clay bodies is distinctly better — by a factor of in between 1.5 and 1.8 — than the corresponding performance of bodies made up of conventional ball clays (Table 1). This fact ensures many advantages:

- low risk of damages to unfired tiles during their turning upside down and transportation along the manufacturing line;

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