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Preparation of pozzolanic addition by mechanical treatment of kaolin clay

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ABSTRACT

Batches containing 5 kg of Serbian medium-quality kaolin clay were mechanically treated in a conventional ball mill for 10, 30, 60, 120, 600 and 1200 min of milling time. High reactive pozzolanic addition was obtained as a result of a number of physicochemical changes induced by milling, namely particle size reduction, specific surface area increase, amorphization/dehydroxylation of kaolinite phase and homogenization of clay constituents. The main characteristics of the pozzolanic material obtained after 1200 min of milling were: median particle size of 6.35 μm, specific surface area of 21.75 $m^2 g^{-1}$, total pore volume of 0.0580 $cm^3 g^{-1}$, pozzolanic activity (compressive strength) of 14 MPa, and reactive silica content of 33.3 wt.%. Continuous increase of pozzolanic activity, despite the agglomeration of particles that was accompanied with specific surface area decrease when milling time was prolonged, could be explained by kaolinite amorphization as well as the mechanical activation of quartz.

1. Introduction

There is an ongoing interest to utilize kaolin clay in construction industry, primarily as a supplementary cementitous material (Wild et al., 1996; Sabir et al., 1996; Caldarone et al., 1994; Shvarzman et al., 2003). Conventionally, special grade kaolin clay is used for the production of white cement clinker and subsequently, white cement. A recent development comprises the use of kaolin clay for production of metakaolin, an artificial pozzolanic addition for cement-based systems. Metakaolin is conventionally manufactured by thermal activation (calcination) of purified high-grade kaolinite at 650–850 °C (Shvarzman et al., 2003). The main beneficial effect of metakaolin in concrete and cement systems is related to its high pozzolanic activity, i.e. its ability to react with portlandite ($Ca(OH)_2$) released during the hydration of Portland cement.

Nowadays, scientists and engineers are searching for possibility to produce pozzolanic additions that, beside technical advantages, have lower influence on the environment and might be produced on lower expenditures. A number of techniques have been developed to alter physical, chemical, structural and surface properties of kaolin clay with a goal to expand or improve its applications. The treatments include (a) calcination at different temperatures (Murray, 1999), (b) application of ionic and/or polar surfactants to turn its hydrophilicity into hydrophobicity or organophilicity (Murray, 1999), (c) amorphization by milling (Aglietti et al., 1986), (d) zeolization by treatment with Na, Ca, Mg and K oxides at 100 °C (Murray, 1999), (e) acidification (Vengris et al., 2001) and (f) various combinations of the previous ones (Suraj et al., 1998).

Mechanical treatment by milling is considered to be friendly to the environment. In comparison with the traditional technological procedures the main advantages are: (a) apparent simplicity of the method, in spite of inherently very complex phenomena that occur during milling; (b) ecological safety, resulting from excluding the operations that involve the use of solvents; and (c) the possibility of obtaining a product in a metastable state, which is difficult (or impossible) to obtain using traditional technological methods (Avvakumov et al., 2002; Boldyrev, 2006; Balaž, 2008).

The effect of milling on the structural changes of kaolin clay has been the subject of a significant number of papers published in recent years (Aglietti et al., 1986; Gonzalez Garcia et al., 1991; Kristóf et al., 1993; Sugiyama et al., 1994; Suraj et al., 1997; Miyazaki et al., 2000; Sánchez-Soto et al., 2000; Frost et al., 2001b; Frost et al., 2001a; Makó et al., 2001; Dellisanti and Valde, 2008; Perrin-Sarazin et al., 2009; Vizcayno et al., 2010; Valášková et al., 2011; Dellisanti and Valde, 2012). The mechanical treatment was found to reduce particle size and increase the specific surface area in the first stage of milling, whereas prolonged milling causes particle agglomeration associated with particle size increase and specific surface area decrease. As a result of gradual structural disordering, dehydroxylation accompanied by partial or complete amorphization of kaolinite phase also takes place.

The properties of clays vary considerably, and are largely dependent on their mineral structure and composition. The main characteristic that

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determines the utility of kaoline clay for various applications is its purity, namely level of various impurities like quartz, anatase, rutile, pyrite, siderite, feldspar, etc. For particular application as pozzolanic addition, a weight loss of higher than 8% would correspond to kaolin of higher quality with more than 65% of kaolinite, whereas kaolin clay with a weight loss of 5–8% (kaolinite content of 40–65%) may be classified as medium quality raw materials still suitable for manufacturing the pozzolanic additives (Aras et al., 2007).

In Serbia, kaolin clays are mainly used for processing ceramic products, although there are high quality deposits, which can be used for other applications, i.e. to obtain a highly reactive pozzolanic addition—metakaolin (Ilić et al., 2010). Kaolin clay located in "Garaši" basin (Aranđelovac area) is endowed with a large deposit of about 55 million tons, not yet exploited.

Investigation presented in this work has been carried out to assess a possibility for obtaining pozzolanic additions by mechanical treatment of the natural kaolin clay deposit "Garaši." This clay is mainly composed of kaolinite and quartz, and, as the effect of quartz on pozzolanic activity induced by milling is not well understood, this study is also an attempt to expand knowledge of the influence of the milling on the morphological and physicochemical changes on the clay rich in quartz. It should be pointed out that the most of the reported studies were focused on the mechanical treatment of small quantities of kaolin clay (typically few to several tens of grams). In fact, since the phenomena that occur during milling are extremely complex, it is not possible to reliably predict the behavior of the material subjected to milling. Consequently, scaling up and/or converting the milling parameters from one to other type of mill is uncertain (Zdujić, 2006).

Therefore, the purpose of this study is twofold. First is to investigate mechanical treatment of kaolin clay in conventional ball mill, which, although usually classified as low-energy mill, with its simple construction allows large amounts of material to be treated. Second, our intention was to mechanically activate medium quality kaolin clay in sufficient quantities that are required for further tastings in cement-based systems, i.e. to determine the pozzolanic activity by flexural and compressive strength measurements.

2. Materials and methods

2.1. Properties of the starting clay

The clay was collected from the exposed faces of the "Garaši" mine (Serbia). Representative clay samples were made from the initial materials using the quartering method. Before being characterized and milled, the samples were dried to less than 0.5% moisture content.

Chemical composition, determined by X-ray fluorescence (XRF) analysis, is given in Table 1. The major mineral constituents are kaolinite [$Al_2Si_2O_5(OH)_4$] and quartz [SiO_2] accompanied with small amount of feldspar [$(K,Na)Si_3O_8$] and mica [$AlSi_2O_6(OH)_2$]. Based on characteristic XRD peaks of each mineral in combination with the chemical analysis the estimated content of kaolinite and quartz was about 51.5 and 40.6 wt.%, respectively. The structural order in starting kaolin is estimated by XRD profile fitting procedure in 18–23° 2θ range of the characteristic kaolinite 020, $1\bar{1}0$ and $11\bar{1}$ reflections. Thus, Hinckley (HI) or Aparicio–Galán–Ferrell (AGFI) index, as a quantitative measure of structural order, were calculated by the procedure described in literature (Chmielová and Weiss, 2002). The values of HI = 0.6 and AGFI = 0.5 indicate highly disordered kaolin.

Table 1
Chemical composition of the starting kaolin clay.

Component	Content (wt.%)	Element	Content (wt.%)
SiO_2	64.57	Si	30.06
Al_2O_3	20.26	Al	10.72
Fe_2O_3	1.07	Fe	0.37
CaO	0.63	Ca	0.45
MgO	0.46	Mg	0.28
Na_2O	0.40	Na	0.30
K_2O	4.46	K	3.70
TiO_2	1.60	Ti	0.96
Loss on ignition (LOI)	6.35		

2.2. Milling procedure

Dried kaolin clay was mechanically treated using a conventional horizontal ball mill. A cylindrical steel vial of inner diameter 360 mm and height 340 mm (volume 0.0346 m^3) filled with hardened steel balls of 20–60 mm diameter was used as milling media. The total weight of the balls was 50.9 kg, so that the balls-to-powder mass ratio was about 10. The angular velocity of a vial was 4.8 s^{-1} (46 rpm). In each milling run, 5 kg kaolin clay was milled for 10, 30, 60, 120, 600 and 1200 min.

2.3. Characterization

2.3.1. Particle size laser distribution (PSLD)

The particle size distribution was measured by laser particle size analyzer (PSA) on Mastersizer 2000 (Malvern Instruments Ltd., UK), which covers the particle size range of 0.02–2000 μm.

2.3.2. Specific surface area (S_{BET}) and porosity

Specific surface area and pore size distribution in the micropore (0–2 nm), and mesopore (2–50 nm) ranges were determined by nitrogen adsorption/desorption isotherms measured with a Micromeritics ASAP 2020-type instrument on samples previously outgassed 10 h in vacuum at 180 °C. Specific surface area, S_{BET}, was calculated using the BET (Brunauer–Emmet–Teller) method from the corresponding nitrogen adsorption isotherm. Total volume of the pores, $V_{pore,total}$, was determined on $p/p_0 = 0.998$, volume of mesopores, $V_{meso,pore}$, using desorption isotherms by BJH (Barrett–Joyner–Halenda) method and volume of micropores using Dubinin method. Maximal pore diameter, D_{max}, was calculated from relationships dV/dw ($cm^3/g{\cdot}nm$) − dw (nm), where V is a pore volume and w pore width.

2.3.3. SEM/EDS analysis

The morphology and elemental chemical analysis were examined by scanning electron microscope (JEOL JSM-6460 LV) equipped with an energy dispersive X-ray spectrometer (LINK AN 1000 EDS microanalyzer).

2.3.4. X-ray powder diffraction (XRD)

The X-ray powder diffraction data were collected on a Philips PW1050 diffractometer using Cu-Kα graphite-monochromatized radiation (λ = 1.5418 Å) in the 2θ range 4–65° (step-length: 0.02° 2θ, scan time: 5 s). The working conditions were 40 kV and 20 mA.

2.3.5. FTIR spectroscopy

Fourier-transform infrared (FTIR) measurements were performed on a BOMEM (Hartmann & Braun) spectrometer on the solid sample prepared using KBr pressed-disc technique over the wave number range of 4000–400 cm^{-1}, with 4 cm^{-1} resolution.

2.3.6. DSC-TGA analysis

Thermal behavior was investigated from the room temperature up to 1100 °C using an SDT Q600 simultaneous DSC-TGA instrument (TA Instruments) with a heating rate of 20 °C min^{-1} under a dynamic (100 cm^3 min^{-1}) N_2 atmosphere.

2.3.7. Pozzolanic activity and reactive silica (SiO_2) content

Pozzolanic activity was determined according to the standard method SRPS B.C1.018, 2001). The mortars were prepared by mechanical mixing of hydrated lime, kaolin clay milled for various milling times,