Thermochimica Acta 580 (2014) 38–45

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal and mineralogical characterization of loess heavy clays for potential use in brick industry

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ARTICLE INFO

Article history:
Received 2 August 2013
Received in revised form 23 January 2014
Accepted 27 January 2014
Available online 10 February 2014

Keywords:
Loess deposits
Thermal analysis
Brick industry

ABSTRACT

This paper describes a study of 11 selected samples of loess soil from Serbia, by using differential scanning calorimetry, simultaneously with thermogravimetry and its differential calculation, known as simultaneous thermal analysis (STA). This survey is supplemented by chemical and mineralogical analysis, particle size distribution, and plasticity and drying susceptibility tests. Correlation analysis of major oxides content and certain technological test results were used for better understanding of the raw material composition and product physical properties. The results indicate that the samples were rich in carbonates, with the highest content of alevrite fraction and variable content of clay-sized particles. Mineralogical analysis confirms significant correlations between major oxides content and reveals that the most common non-clay mineral present is quartz, followed by calcite, dolomite and sodium feldspar. Major clay minerals include illite, chlorite, smectite and, in some cases, low quantities of kaolinite. Although STA method is well-known, this is the first time that it was used for discussion about its practical aspect, for characterization of the loess deposits, in terms of exploitation in brick industry.

1. Introduction

North Serbia region is mostly occupied by quaternary sediments, which consist of sand, gravel, alevrites and clay, within river and swamp sediments. Loess sediments have been used in brick industry for decades, and are therefore named “brick soil”. Lower and older loess sediments are characterized by forest or savannah-like soil, while upper soil horizons are stepic soil dominant. Loess can be extremely sandy or highly plastic, but usually quality varies within one deposit. Loess has been deposited in the Pleistocene cold period (glaciation). During warmer seasons, when it came to loess sediments deposition interruption (interglaciation), change in the already deposited material occured due to fossil (buried) soil creation. The number of layers buried indicates the number of interruptions in creation and deposition of loess sediments. Buried soil contains a lot of clay minerals, it is compact and red to brown in color. These layers are important in brick industry because they carry clay minerals that increase plasticity. Brick factories whose mines contain several layers of buried soil produce hollow clay bricks. Swamp loess can be also used in manufacture of roof tiles, because of increased content of clay minerals. Hollow clay products made of loess have thick walls, high volume mass and therefore require more energy upon thermal treatment [1–3].

Geologically, North Serbia is mainly covered in loess deposits that have some common features: yellowish colour, uniform size and similar composition. The most abundant component of these heavy clays is silt (up 80 wt%). Alternation of silty loess layers with clay in North Serbia shows that the origin of the material is a combination of eolian (wind impact) and fluvial (brought by waterways). Loess deposits in Serbia originated as a response to tectonic formation of the Panonian basin and increased sediment supply from rivers [1–3].

Deposits composition is of quartz, carbonates and clay minerals. Quartz exists in almost all brick clays. Fine-grained sand, present up to a certain percentage, does not interfere with brick production, but its presence as quartzite in the form of pebbles or fragments of terrace origin is undesirable. Sandstone is the most common in diluvial sediments, in the form of pieces of different size. Quartzite and sandstone with their abrasiveness show destructive effect in primary production line, especially on the mouthpiece of extruder presses. Quartz sand, especially the one of coarse grit, abrasively affects equipment, and can, as well as other forms of quartz mineral, adversely affect the mechanical properties of the final product, if the cooling process is inadequatelly executed. Transformation from α into β quartz form at 573 °C, causes mechanical damage due to the increase in volume of about 2%. The β–α change occurs readily on cooling. Although quartz is not stable above 870 °C, changes

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0040-6031/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2014.01.026

occur so slowly that bricks fired above 1000 °C usually still contain α quartz when examined cold. Loess contains a considerable amount of carbonates (calcite, and to a lesser extent dolomite), even up to 35 wt%. In some deposits, calcite can exist in the form of strips or small tiles, which together with concretions ("loess dolls"), can destroy a brick product. If carbonates are finely dispersed and uniformly distributed, they react in firing process with clay minerals and form calcium silicates, which improve mechanical properties. Having this in mind, preparation of loess raw materials should include grinding below 0.5 mm to avoid harmful effects of lime "popcorns" on the final product. In terms of mineralogical composition of clays, deposits are somewhat heterogeneous, with montmorillonite as a dominant component and sometimes illite, chlorite and kaolinite [1,2,4,5].

Thermal analysis is often used to detect changes of physical parameters as a function of temperature in different materials. In ceramics, this technique is used for the initial characterization of components, study of firing processes, mineralogical composition analysis and determination of fired ceramic material properties. Thermal analysis methods are well established in the science of clay and related industrial applications. Manufacturers use these techniques in factories to optimize production process [6]. The major heavy clay material constituents, including carbonates, sand, clay and moisture, all undergo thermal reactions when heated. Thermal stability of any material is related to its chemical and surface properties. For example, clays of very small particle size tend to decompose more easily than more coarsely grained clays [4]. Reactions and temperatures at which reactions occur can be determined by differential thermal analysis (DTA) or differential scanning calorimetry (DSC). Problems with application of thermal analysis can arise if exothermic peaks are superimposed on endothermic peaks associated with clay, sand and silt fractions [7]. Changes in sample mass detected using thermo gravimetric (TG) analysis could be associated with the following processes: oxidation, reduction, and loss of adsorbed structural water, thermal decomposition followed with the release of gaseous or volatile liquid products, combustion in air atmosphere or bonding gases from atmosphere in non-volatile products. Temperatures at which these reactions occur are characteristic of certain minerals, and are used for identification and determination of their presence in a sample. TG analysis is most commonly used for identification of clay minerals and carbonate decomposition, but it cannot be used to detect melting, while melting and decomposition cannot be distinguished unambiguously using DTA. A substance which melts with accompanying decomposition must thus be studied using some comparative method, such as DTA or DSC [8,9]. Endothermic effects occur as a result of phase transformation, dissociation, dehydration, dehydroxilation, reduction, evaporation, sublimation, and exothermic effects are caused by oxidation (combustion of organic matter, sulfide oxidation, and oxidation of iron ions). Endothermic or exothermic effects occur during melting, decomposition or crystallization of crystal lattice, redox reaction and reaction in the solid phase [8]. Since simultaneous endothermic and exothermic mass loss transformation may be present during thermal analysis, the derivative of TG curve (DTG) is used as more indicative to several decomposition steps in clays then DTA or DSC. DTG curve shows changes in TG slope that may not be obvious from TG curve. As DTG curves represent the total mass loss rate during all the occurence of the endo- and exothermic decompositions, they allow a better evaluation of these simultaneous transformations from their respective DTG peaks [10,11].

Loess soils were not sufficiently analyzed in terms of application in brick industry [1,2,12], and the aim of this paper is to provide their characterization based on simultaneous thermal analysis complemented with chemical and mineralogical data, as well as particle size distribution, plasticity and drying susceptibility tests.

2. Materials and methods

2.1. Characterization of loess samples

Samples were collected bellow maximum 60 cm of depth, to exclude levels containing high amount of vegetable matter and chernozem, disturbed by agricultural activity. The samples were taken in North Serbia (Vojvodina): Čelarevo (CE1 and CE2), Debeljača (DB), Golubinci (GO), Iđoš (ID), Inđija (IN1 and IN2), Senta (SE), Banatsko Karađorđevo–Žitište (ZI), Bačko Petrovo Selo (BP) and Crvenka (CR).

Major elements content is determined using classical silicate analysis [12], while all the measurements were performed in triplicates.

The mineralogical analysis is carried out by X-ray diffraction (XRD) using a powder diffractometer (Philips PW-1050) [1]. For a better characterization of constituent clay minerals, XRD analysis was carried out on the <2 μm fraction in which different clay minerals are more clearly recognized. In particular, X-ray investigation was carried out on randomly oriented samples and also on glycolated and heat treated oriented samples.

Particle size distribution (PSD) was determined by granulometry analysis (pipette method), as described in literature [1].

Pfefferkorn method was used to determine the plasticity of moistened mass [13]. After shaping of tiles in a laboratory extruder press, moist samples are used to obtain drying susceptibility of heavy clays, by using a barelattograph to trace the Bigot's curve [14].

CO_2 content analyses were carried out by simple volumetric technique to constrain the amount of total carbonates present. The test is done using Scheibler calcimeter, with 3 vol% HCl, when carbonates from raw dry material react and the volume of CO_2 is measured. The result is calculated as a share of carbonates in the sample, without determination of the origin (Ca, Mg, Na, Fe, etc.). Carbonates content can be determined also by firing to 1000 °C (loss on ignition), but at the same time the result gives the content of burnable organic components [8,15].

2.2. Statistical analysis

Major oxides contents and technological characteristics of loess clays are tested for independency, using two-tailed Pearson correlation analysis by program StatSoft Statistica, v.10 for Windows. The results are presented in a table, as a correlation coefficient, *r*.

2.3. Simultaneous thermal analysis

The DSC-TGA-DTG curves were obtained using a SDT Q600 (TA Instruments) device with platinum/platinum-rhodium thermocouple. The temperature of the air-dried samples was raised from room temperature to 910 °C under air atmosphere with heating rate of 20 °C/min. The sample mass varied between 6 and 16 mg, and samples were weighed in platinum pans. A small amount of samples allowed better resolution of peaks and faster heating [8].

3. Results and discussion

3.1. Loess soils chemical and mineralogical composition

The chemical composition of materials used is presented in Table 1, with LOI (loss on ignition) and CCC (total carbonates content determined by calcimeter). Pearsons's correlations between these parameters are shown in Table 2. Results and conclusions are supported with X-ray diffraction experiments (Table 3).

Table 3 According to SiO_2 and Al_2O_3 content, the highest clay content has been obtained in sample BP, and the lowest in ID.