Research paper

Red-clay ceramic powders as geopolymer precursors: Consideration of amorphous portion and CaO content

Martin Keppert[a], Eva Vejmelková[a], Petr Bezdička[b], Magdaléna Doleželová[a], Monika Čáchová[a], Lenka Scheinherrová[a], Jaroslav Pokorný[a], Martin Vyšvařil[c], Pavla Rovnaníková[c], Robert Černý[a,*]

[a] Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Prague 6, Czech Republic
[b] Institute of Inorganic Chemistry AS CR v.v.i., Husinec – Řež 1001, 250 68 Řež, Czech Republic
[c] Institute of Chemistry, Faculty of Civil Engineering, Brno University of Technology, Žižkova 17, 602 00 Brno, Czech Republic

A B S T R A C T

Geopolymers are conventionally prepared from metakaolin, fly ash, or blast furnace slag. In this paper, geopolymer synthesis using two different red-clay ceramic powders and a varying amount of Na_2O/SiO_2 activator is presented. Experimental results show that despite of the high content of crystalline minerals and lower concentration of amorphous matter, both tested precursors enable to prepare geopolymers with satisfactory mechanical properties. The discussion of measured values of compressive strength with respect to SiO_2/Al_2O_3 and $Al_2O_3/(Na_2O + K_2O)$ ratios in the prepared geopolymer mixes reveals that the consideration of only amorphous portion of ceramics is appropriate. A higher content of CaO in the precursor is found to cause a broader pore size distribution and higher porosity of resulting geopolymers, which is due to the formation of calcium silicate hydrates.

1. Introduction

Geopolymers (or aluminosilicate inorganic polymers, alkaline activated materials) are materials synthesized from a suitable aluminosilicate precursor (i.e., monomer) by polymerization induced in alkaline environment. The prepared materials consist of fundamental SiO_4 and AlO_4^- structural units connected through oxygen bridges (e.g., poly (sialate) structure $-Si-O-Al-O-$) to polymer network (Brus et al., 2016). Since the AlO_4^- unit is negatively charged, the presence of cations in the structure is necessary. The geopolymer synthesis, in a simplified way, lies in: 1) dissolution of aluminosilicate precursor in alkaline activator; 2) polycondensation of monomers to the final polymer network; 3) solid state transformation to final hard solid (Yun-Ming et al., 2016). As activators, a wide range of alkaline solutions is applied: NaOH, Na_2CO_3, sodium silicate (water glass), sodium aluminate, or their potassic or lithic equivalents (Hosan et al., 2016; Peys et al., 2016; Hu et al., 2017). The "overall" composition of the geopolymer can be described as follows (Davidovits, 1991): $nM_2O\cdot Al_2O_3\cdot xSiO_2\cdot yH_2O$ where M is Na, K, or Li, n ranges between 1 and 1.6, y between 3 and 7 and x is higher than 2 (or, the Si/Al molar ratio is higher than 1). Obviously, the formula is applicable just for geopolymers which do not contain CaO and MgO. Traditionally, geopolymers are supposed to be first of all an alternative to Portland cement based

materials with possible environmental and durability benefits (which are paid by more sensitive mix design and technology, as compared to ordinary Portland cement). Nevertheless, geopolymers can also be used in other applications, frequently advantaging their thermal stability: for production of thermally resistant construction elements, as adhesives, for solidification of hazardous wastes, or as catalyst support (Pacheco-Torgal et al., 2014; Topçu et al., 2014; Lemougna et al., 2016; Kovarik et al., 2017; Provis, 2017).

There is a wide range of possible aluminosilicate precursors of geopolymers, as well as activation solutions; obviously the most important geopolymer properties (setting/hardening kinetics, strength) depend, besides other, on the composition of both principal raw materials. Probably the most widely studied aluminosilicate precursor of geopolymers is metakaolin (dehydroxylated kaolin, MK). As the raw material, either quarried clay or an industrial clayey waste (sludge from paper or ceramics production) is used. The optimum calcination temperature depends on the composition of particular clay and ranges from 600 to 900 °C (Rashad, 2013; Mohammed, 2017). The initial crystalline structure of present clay minerals is disrupted during the dehydroxylation and the material becomes reactive; obviously the higher level of dehydroxylation (i.e., the amorphousness of the material) results in better reactivity. The mechanochemical treatment of clay is also possible (MacKenzie et al., 2007; Yun-Ming et al., 2016). The important

Table 1
Selected parameters of metakaolins for geopolymer synthesis.

Ref.	Content (wt%)		d$_{50}$ (um)	S$_g$ (m^2/g)
	SiO$_2$	Al$_2$O$_3$		
Kovarik et al., 2017	52.1	41.9	4.0	13.0
Borges et al., 2017	54.5	44.2	4.5	N/A
Belmokhtar et al., 2017	53.6	42.2	4.8	6.2
Lahoti et al., 2017	53.0	43.8	1.3	N/A

Table 2
Composition of geopolymer mixes.

Geopolymer	RCC (g)	Water glass (g)	NaOH (g)	Water (g)
H/L1	200	70	2.57	41
H/L2	200	80	2.95	36
H/L3	200	90	3.33	31

parameters of several calcined clays successfully used for geopolymer synthesis are summarized in Table 1. Concerning the phase composition, metakaolin is usually believed to be fully amorphous, but it can contain some crystalline residuals (kaolinite, muscovite, quartz, etc.) (Belmokhtar et al., 2017). Other frequently used aluminosilicate precursors are coal fly ash (FA) and ground granulated blast furnace slag (GGBS). The most important difference compared to MK is content of CaO which in FA varies widely from 0 up to 16.5% (Reddy et al., 2016). GGBS contains significantly higher amounts of CaO (30–40%) and MgO (5–10%) (e.g. Fiala et al., 2017). FA and GGBS contain just minor amount of crystalline minerals (< 20%, the most abundant are quartz and mullite) (Font et al., 2010; Poole and Sims, 2016), the rest of material is glassy. A geopolymer derived from GGBS and FA contains both calcium silicate hydrates and "true geopolymer" structures (Li et al., 2010).

In this paper, a relatively unusual aluminosilicate precursor, namely red-clay ceramic grinding dust (RCC), which is an industrial by-product generated in brick blocks calibration, is used for the preparation of geopolymer mixes. The fundamental properties of two different RCC are determined at first and compared with conventionally used aluminosilicate precursors. Then, the properties of obtained geopolymers are analyzed, taking into account the precursors' amorphous portion and CaO content.

2. Experimental methods

Two kinds of red-clay based ceramic powders were used as geopolymer precursors. They were generated as by-products of the calibration of thermal insulating brick blocks and will be marked H and L in what follows, according to the brick factories placed in Hevlin and Libochovice localities (Czech Republic). The RCC powders were used as-received, just the particles larger than 1 mm were removed by sieving. The chemical composition of ceramic precursors was examined via X-ray fluorescence (XRF) spectroscopy, using a Thermo ARL 9400 XP instrument. The obtained data were evaluated by Uniquant 4 software. Diffraction patterns were collected using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Co$_{K\alpha}$ radiation, 40 kV, 30 mA, line focus) and a multichannel detector X'Celerator with an anti-scatter shield. X-ray patterns were measured in the range of 5 to 105° 2 Θ with a step of 0.0167° and 1000 s counting per step. Conventional Bragg-Brentano geometry was used with the following parameters: 0.02 rad Soller slit, 0.5° divergence slit, 1.0° anti-scatter slit, and 15 mm mask in the incident beam, 5.5 mm anti-scatter slit, 0.02 rad Soller slit and Fe beta-filter in the diffracted beam. Side loaded sample holders were used to minimise the preferred orientation. The duration of the scan was ca. 13.2 h. Quantification of the experimental data was performed with the similar methodology as described by Hradil et al. (2017) using the Rietveld method. The BGMN code was used for all calculations (Bergmann et al., 1998). This program includes a code which permits the use of structural models describing correctly the disorder appearing frequently in the case of clay minerals (Ufer et al., 2004, 2008). Models of other reference materials were described as standard Rietveld models (ICSD, 2017). Refined parameters comprised unit cell parameters for all phases as well as size and micro-strain broadening parameters. Preferred orientation was refined only for mica

(muscovite, illite). Spherical harmonic of the 2nd degree was used (Bergmann et al., 2001). Additional refined non-structural parameters were sample displacement error and a 6th degree polynomial for background modelling. The amorphous portion of the materials was quantified by help of added internal standard (ZnO) as described, e.g., by Madsen and Scarlett (2008). Zinc oxide was chosen as an internal standard as its presence is not expected in all studied materials (no Zn was found by the XRF spectroscopy). The particle size distribution was determined using a laser diffraction analyzer (Fritsch, Analysette 22 MicroTec plus). Density of RCC powders was measured by helium pycnometry (Pycnomatic ATC). Their pore system was characterized by help of the nitrogen adsorption method (Sorptomatic 1990); the specific surface area was determined by the BET method, the pore size distribution by the BJH method. The RCCs were also examined by TG/DSC analysis (Labsys Evo, Setaram).

Geopolymers were prepared from the H and L precursors, with three dosages of activating solution (Table 2) based on sodium water glass VS 1.6 (Vodní sklo, a.s., Czech Republic) and NaOH (p.a., Penta Chemicals, a.s., Czech Republic). The silicate modulus of the activator was kept constant (1.4); the water content – sum of dosed waster and water present in sodium silicate solution – was also equal in all mixes. The recipes were based on preliminary experiments performed with varying activator composition and dosage. The varying dosage of liquid activator means varying Si/Al and Na/Al ratio in the prepared materials. The mixed geopolymer paste was placed to 40 × 40 × 160 mm moulds, covered by foil in order to prevent fast drying and cured in laboratory conditions (23 °C) for 28 days.

The flow properties of pastes were characterized by help of a Discovery HR-1 (TA Instruments) hybrid rheometer and TRIOS 4.0.2.30774 software for data evaluation. In order to avoid wall slippage, the building material cell and the paddle type rotor was adopted. The gap thickness was chosen to be large enough (10 mm) for paste dispersion. All the measurements were done at 25 °C. The mixed paste was pre-sheared for 60 s at 100 s^{-1} in order to re-homogenize the sample and to eliminate its shear history. After a period of rest of 60 s, the rheological measurements were started. The testing routine comprised a shear rate increase (from 0.1 to 100 s^{-1}) applied through 30 steps with 15 s of measuring time at each shear rate, followed by a decrease of shear rate at the same conditions. The flexural strength (3 replicates) was measured by three point bending test (EN 196-1); the compressive strength was determined by help of halves of prisms after bending test (i.e., 6 replicates). The strength measurements were performed by an FP 100 testing device (Heckert). The density, bulk density, and porosity were determined by help of helium pycnometry (Pycnomatic ATC) and volume determination of prismatic samples (from moulds 40 × 40 × 160 mm).

3. Results

3.1. Characterization of RCC precursors

The chemical composition of RCC is summarized in Table 3. The line "total" means chemical composition, as it was determined by XRF. The XRD analysis of RCC (Fig. 1, Table 4) revealed a high complexity of these materials; the dominating mineral was quartz, followed by numerous silicates which were partially contained in the loess and partially synthesized during the ceramics firing. Terms microcline and