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Research paper

The identification of geopolymer affinity in specific cases of clay materials

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ABSTRACT

The article describes a synthesis of a geopolymer matrix based on a specific raw material – thermally treated shale – a waste material from mining activity. The intensity of the thermal treatment has been studied by solid-state ²⁷Al nuclear magnetic resonance. The amount of 38–54 wt.% of aluminum ions in tetra-coordination, according to the sampling point, signals the possibility of converting the waste material into a solid geopolymer matrix. A mineralogical analysis has specified that this value corresponds to the aluminum ions involved in two different shale components: the amorphous clayed residues and a mullite phase. In spite of the high content of mullite and quartz, the amorphous clay residues in the shale react with an aqueous alkaline solution and create stable solids which have shown excellent mechanical properties. The character of the geopolymer bonds has been investigated by infrared spectroscopy, which has proven the presence of geopolymer chaining and distinguished them from mullite wavenumbers. The obtained results have confirmed that the shale could be used as a new raw material for geopolymer synthesis.

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1. Introduction

Geopolymers are materials known since 1979, when they were first named by Davidovits (1991). The origin of geopolymers has been described by many authors (Alonso and Palomo, 2000; Xu and van Deventer, 2000; Lee and van Deventer, 2003; Davidovits, 2008). Thermally activated alumino-silicate minerals react with a highly alkaline solution at ambient temperature. One of the conditions of this reaction is the presence of a tetra- or penta-coordinated aluminum ion ([4] Al³⁺, [5] Al³⁺), acquired by the thermal activation of clay materials (Sanz et al., 1988). Besides the thermal activation of clay materials, the effects of the ²⁷Al coordination changes were identified in the ashes of coal burning (fluid-burning technology) and in other materials with the position of [4] Al³⁺ and/or [5] Al³⁺ (Phair et al., 2004; Duxson et al., 2007; Yunsheng et al., 2007; Buchwald et al., 2009). Only a tetra- and penta-coordinated aluminum ion could be hydrated in an aqueous alkaline solution and could create a connection with the conformable coordinated silicon through oxygen. This reaction is called geopolymerization and creates polymeric –Si–O–Al– bonds well-ordered in a three-dimensional network. The ratio of silicon and aluminum tetrahedrons influences the properties of the geopolymers, e.g. a higher content of silicon tetrahedrons than the classical rate (1:2) in kaolin improves the compressive strengths of the final solid (Davidovits, 1991, 2008). The negative charge of an alumina tetrahedron is balanced by the presence of alkali or alkaline-earth metal ions, commonly Na⁺, K⁺ or Ca²⁺.

There is a wide, still increasing, spectrum of source materials suitable for a geopolymerization including waste materials as well. The raw materials used the most often are calcinated kaolins (pure and high-quality) with a significant component of the kaolinite mineral (Duxson et al., 2007; Davidovits, 2008; Medri et al., 2010; Yunsheng et al., 2010), coal fly ashes (Phair et al., 2004; Criado et al., 2007) and blast-furnace slag (Yunsheng et al., 2007; Fu et al., 2011). Chindaprasirt et al. (2009) prepared coal-bottom-ash geopolymer and Songpiriyakij et al. (2010) following new trends in the combustion of alternative fuels made a geopolymer based on biomass ashes. It was also found that non-used kaolinitic clay in the ceramic industry (Perna et al., 2006) and ceramic waste material so-called “white water” containing only a certain proportion of the clay component could be exploited (Hanzlíček et al., 2006). In many countries the alternative raw materials for the geopolymerization are still being searched and applied, for example natural zeolites (Villa et al., 2010), calcinated paper sludge (Antunes Boca Santa et al., 2013), rice husk ash (Bouzáon et al., 2014), lignite bottom ash (Sathonsaowaphaka et al., 2009), etc.

The essential property of the finally formed 3D net is that this network could accept many different kinds of additives including waste materials. The structure and properties of the geopolymer are affected by the type, quality and amount of the additives. Some (active) additives, especially ashes and slag, are directly chemically bonded into the formed net, whereas the others (non-active) are encapsulated into the geopolymer net (Davidovits, 1991, 2008). Other main properties of the geopolymer are a high early strength, excellent mechanical properties, acid and alkali resistance, compact microstructure, low porosity, fire and heat resistance, low leaching ability and freeze–thaw resistance (Davidovits, 1991, 2008; Palomo et al., 1999; Roy, 1999; Xu

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and van Deventer, 2000; Duxson et al., 2005; Yunsheng et al., 2007; Zhang et al., 2008; Fu et al., 2011).

The properties mentioned above predetermine its practical utilization: geopolymer cement, construction or composite materials (Perna et al., 2010), materials for the renovation and restoration of historical monuments (Hanzlicek et al., 2009), fire-resistant materials (Davidovits, 1991, 2008), the fixation of heavy metals (Phair et al., 2004; Yunsheng et al., 2007), the inhibition of hazardous material (Guangren and Yuxiang, 2002; Zhang et al., 2008; Perna and Hanzlicek, in press) and many other applications (Perna et al., 2009).

The main aim of this article is to find a new source of a material for a geopolymerization and to verify properties of a solid geopolymer matrix. The tested material was the shale from the Zbuch deposit (West Bohemian region, Czech Republic). The coal mining in the area leaves behind a large number of dumps of the extracted material. This specific material contained a proportion of coal which has been slowly burning over the last 50 years. The coal burning was sufficient for the thermal activation of the shale, which naturally changed the aluminum-ions coordination. The focus of this work is a verification of the aluminum-ion transformation and a determination of the possible utilization of this waste material.

2. Materials and experimental procedure

2.1. Materials

This specific waste material formed multiple layers over the coal veins and was extracted and heaped beside coal-mining installations. The remnants of coal in this material and the contact of the stacked material with air, humidity and pressure initiated slow coal burning. Long-term exposure to elevated temperature naturally changes the coordination of aluminum ions, like the thermal treatment of clay materials obtained by clay calcination. The clay substances were hence “activated” or naturally transformed by the effect of self burning. The thermal treatment of the clay double-layer minerals generally means “activation” or shift of the [6] Al³⁺ ions in their active or meta-stable [5] Al³⁺ position to the oxygen. When the changes in aluminum coordination could not be determined by the controlled temperature, we labeled the material as naturally activated, even though the activation was a consequence of a previous coal-mining activity.

The naturally activated shale from the above-mentioned region was used. In this large deposit area (800 × 600 m), samples were taken in a quantity of 5 kg from three different parts of the heaped shale. The sampling points were more than 300 m apart, and the points selected also differed in the color of the material – from light to dark red. The material obtained at each sampling point was homogenized and the amount was reduced by quartering for the subsequent analyses. The average chemical compositions are presented in Table 1 (L.O.I. – loss on ignition).

2.2. Sample preparation

The shale was treated in a laboratory dryer for 8 h and then ground by a Retsch friction mill and later by a vibration mill reaching an average diameter around 50%: 8.05–9.93 μm.

The 50 g of milled shale was mixed with an alkaline activator prepared from KOH and soluble potassium silicate. The reaction began in 15–20 min. The homogenized mixture was pulled into prism molds (the EN 196-1 standard size of 40 × 40 × 160 mm), which were covered

by a plastic sheet to retard surface-water evaporation. The molds were placed in the laboratory drier for 3 h (at a temperature of 60 °C). The times for setting and hardening varied because of the different sampling points from 24 h to 5 days. After this period, the samples were removed from the molds and cured at room temperature. The final hardening occurred at laboratory conditions (temperature 25 °C, humidity 55%). The mechanical properties were determined and XRD and IR analyses conducted after 28 days.

2.3. Methods

The chemical analyses were performed by an X-ray-fluorescence (XRF) analyzer (Spectro IQ, Kleve, Germany), where the target material was palladium and the target angle from the central ray was 90°. The focal point was a 1 mm × 1 mm square, and the maximum Anode Dissipation was 50 Watts with 10-cfm forced-air cooling. The tested samples were prepared by the pressed-pellet method.

The solid state MAS-NMR (magic angle spinning–nuclear magnetic resonance) was measured using a Bruker Avance 500 WB/US NMR spectrometer (Karlsruhe, Germany, 2003) in 4-mm double-resonance probeheads at a magic angle spinning (MAS) of $\omega_r/2\pi = 13$ kHz. The ²⁷Al MAS-NMR spectra were acquired at 130.287 MHz, using a tip angle of 20° (1 μs pulse length) with a recycle delay of 2 s. The spectra were referenced to Al (NO₃)₃ (0.0 ppm).

The X-ray diffraction (XRD) examination of the crystallographic phases was performed with an X'Pert PRO θ–θ powder diffractometer with parafocusing Bragg-Brentano geometry using Cu K_α radiation ($\lambda = 1.5418$ Å, generator setting: 40 kV, 30 mA). An ultrafast X'Celerator detector was employed over the angular range 7–70° (2θ) with a step size of 0.017° (2θ) and a counting time of a 20.00 s step⁻¹. The data evaluation was performed using the High Score Plus V 2.2e pANalytical software package, Almelo, Netherlands.

The infrared spectra were measured using the Protégé 460 E.S.P. (Thermo Nicolet Instruments Co., Madison, USA) spectrometer over the range between 4000 and 400 cm⁻¹ at a resolution of 4 cm⁻¹, averaging 128 scans by the ATR technique to minimize disruption to the sample caused by the preparation techniques (Rees et al., 2007). Spectral decomposition (or deconvolution) was performed using the OMNIC 7 program, with a Gaussian function. The starting calculation parameters for the curve fitting process, such as the number of component bands, band positions, width at half-maximum, relative intensities, and shape, were predetermined by the combined procedures of the secondary derivative method and Fourier self-deconvolution.

The strength tests were confirmed by the European Standard Norm EN 196-1 (Methods for Testing Concrete, 2005) using prisms with a standard size of 40 × 40 × 160 mm after 28 days (laboratory temperature and pressure). The tests were executed on an E156 strength motorized press (strain rate 0.6 ± 0.2 MPa/s) with suitable devices (producer: Matest company, Italy). At first, the flexural strength was measured in the three-point bending configuration (support distance 100 mm) with an E172-01 flexural device. Portions of prism 40 × 40 × 160 mm broken in flexure were used for compressive strength determination with an E170 compression device. Three prisms of each sampling point material were tested and the mean and standard deviation reported. Each value for flexural and compressive strength is the average of three or six measurements, respectively.

3. Results and discussion

The chemical analyses of the presented samples are very similar. The low loss on ignition (L.O.I.) in Table 1 shows that the burning of the coal part in the shale was practically finished. From the chemical composition, we could calculate a clayed content of about 49 to 50 wt.%. The XRD analysis of the shale (Fig. 1) confirmed a thermal transformation of the material and showed quartz Q (SiO₂) content as a major phase together with mullite M (3Al₂O₃ · 2SiO₂). The minor phase was a

Table 1
The chemical composition of three shale samples.

Shale/oxide	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	K ₂ O	SO ₃	L.O.I.
Sampling point 1	53.75	30.27	0.81	0.68	5.60	2.56	1.44	2.98
Sampling point 2	54.47	31.41	0.53	0.57	5.59	2.64	0.73	2.00
Sampling point 3	54.69	28.63	0.59	0.62	7.07	3.72	0.73	1.60

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