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ScienceDirect

Waste Management 28 (2008) 416–423

waste management

www.elsevier.com/locate/wasman

Coal fly ash as raw material for the manufacture of geopolymer-based products

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Accepted 1 February 2007

Available online 26 March 2007

Abstract

In this work coal fly ash has been employed for the synthesis of geopolymers. Two different systems with silica/alumina ratios stoichiometric for the formation of polysialatesiloxo (PSS, $SiO_2/Al_2O_3 = 4$) and polysialatedisiloxo (PSDS, $SiO_2/Al_2O_3 = 6$) have been prepared. The alkali metal hydroxide (NaOH or KOH) necessary to start polycondensation has been added in the right amount as concentrated aqueous solution to each of the two systems. The concentration of each alkali metal solution has been adjusted in order to have the right liquid volume to ensure constant workability. The systems have been cured at four different temperatures (25, 40, 60, and 85 °C) for several different times depending on the temperature (16–672 h at 25 °C; 72–336 h at 40 °C; 16–120 h at 60 °C and 1–6 h at 85 °C). The products obtained in the different experimental conditions have been submitted to the quantitative determination of the extent of polycondensation through mass increase and loss on ignition, as well as to qualitative characterization by means of FT-IR spectroscopy. Furthermore, physico-structural and mechanical characterization has been carried out through microscopic observations and the determination of unconfined compressive strength, elasticity modulus, apparent density, porosity and specific surface area. The results have indicated that the systems under investigation are suited for the manufacture of pre-formed building blocks at room temperature.

1. Introduction

Since 1979, when Davidovits first introduced the term ‘‘geopolymers’’ to designate a new class of three-dimensional alumino-slilicate materials (Davidovits, 1979), the interest towards the implementation of new technologies for the manufacture of great potentialities geopolymer-based products has steadily grown.

Geopolymers are also referred to as alkali-activated alumino-slilicate binders and comprise three classes of inorganic polymers that, depending on the ratio of silica to alumina (silica/alumina), are based on the following three different monomeric units: (–Si–O–Al–O–), polysialate (PS), $SiO_2/Al_2O_3 = 2$; (–Si–O–Al–O–Si–O–), polysialatesiloxo (PSS), $SiO_2/Al_2O_3 = 4$; (–Si–O–Al–O–Si–O–Si–O–), polysialatedisiloxo (PSDS), $SiO_2/Al_2O_3 = 6$.

The synthesis of geopolymers takes place by polycondensation and can start from a variety of raw materials. Davidovits (1989, 1991, 1993), Palomo et al. (1992), Barbosa et al. (2000), Cioffi et al. (2003), Kriven et al. (2003), Kriven and Bell (2004) and Schmücker and MacKenzie (2005) made use of metakaolinite to obtain geopolymers by reaction with alkali metal (Na or K) silicate.

Abbreviations: PS, polysialate geopolymer ($SiO_2/Al_2O_3 = 2$); PSS, polysialatesiloxo geopolymer ($SiO_2/Al_2O_3 = 4$); PSDS, polysialatedisiloxo geopolymer ($SiO_2/Al_2O_3 = 6$); NaPSS, system stoichiometric for polysialatesiloxo geopolymer with sodium silicate solution added; KPSS, system stoichiometric for polysialatesiloxo geopolymer with potassium silicate solution added; NaPSDS, system stoichiometric for polysialatedisiloxo geopolymer with sodium silicate solution added; KPSDS, system stoichiometric for polysialatedisiloxo geopolymer with potassium silicate solution added.

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0956-053X/$ - see front matter
doi:10.1016/j.wasman.2007.02.001

Alternatively, Ikeda et al. (1998), van Jaarsveld and van Deventer (1999), Phair et al. (2000), Xu and van Deventer (2000), Xu et al. (2001), Swanepoel and Strydom (2002), Lee and van Deventer (2002, 2004), van Jaarsveld et al. (2002, 2003) and Bakharev (2005) have proven that geopolymers can be obtained starting from many raw silico-aluminates and alumino-silicates, including coal fly ash. Also in this case the polycondensation takes place by reaction with alkali metal silicate.

Whatever the case, the synthesis of geopolymers relies on the same reaction mechanism, as reported by Xu and van Deventer (2000). When in contact with the high pH alkaline solution, the starting materials dissolve and the geopolymers are precipitated.

Amorphous geopolymers are obtained at condensation temperatures ranging from 20 to 90 °C, while crystalline ones are formed in autoclave at 150–200 °C. The structure of crystalline geopolymers resembles that of zeolite A (Davidovits, 1991).

Geopolymeric materials are attractive because excellent mechanical properties and durability can be achieved (Palomo et al., 1992; Davidovits and Davidovics, 1988). Thermal stability and resistance to acid attack are excellent. Schmücker and MacKenzie (2005) have proven that the geopolymer matrix composition is virtually left unchanged upon heating to 1200 °C. Furthermore, due to much lower Ca content, geopolymer-based materials are much more resistant to acid attack than Portland cement-based ones (Bakharev, 2005).

Great interest also derives from the reduced energy requirement for the manufacture of new materials based on geopolymers. In fact, the reaction pathway requires either metakaolinite, obtained by calcining kaolinite at temperatures of 600–700 °C, or raw silico-aluminates and alumino-silicates.

The applications of geopolymer-based materials range within the fields of new ceramics, cements, matrices for hazardous waste stabilization, fire-resistant materials, asbestos-free materials and high-tech materials (Davidovits, 1991; van Jaarsveld et al., 1997, 1999; Kriven et al., 2004; Bell et al., in press).

In this work, coal fly ash has been used for the synthesis of geopolymers of the classes polysialatesiloxo and polysialatedisiloxo in different experimental conditions in terms of temperature and time of polycondensation. The different products obtained have been characterized from the qualitative point of view by means of infrared spectroscopy (FT-IR) and from the quantitative point of view through the measurement of the amounts of alkali metal silicate and water reacted upon polycondensation following an experimental procedure previously developed (Cioffi et al., 2003). Other quantitative measurements have been carried out regarding physico-structural and mechanical properties such as specific surface area, porosity, apparent density, unconfined compressive strength and elasticity modulus. Finally, microstructural observations have been carried out by means of scanning electron microscopy (SEM).

The coal fly ash used in this work comes from an electric power generation plant. Thus, the work is also of interest from the environmental point of view inasmuch as it proposes matter recovery from a residue with the aim to produce good quality materials.

Coal fly ash management is an issue of current concern, as the quantity produced all over the world is so high that the problem of environmentally sound recycling of this residue has not yet found final solution. In fact, international conferences on coal fly ash recycling are currently held and a significant number of papers are found in the recent literature on related topics. To this regard, further information can be found in the Fly Ash Resource Center web site (www.rmajko.com).

2. Materials and methods

The coal fly ash used for the synthesis of the geopolymers was supplied by the Italian electricity board (ENEL) and comes from the power plant located in Brindisi (Southern Italy). Its characterization by means of traditional chemical analysis gave the following chemical composition: SiO_2, 44.3%; Al_2O_3, 20.2%; Fe_2O_3, 10.5%; K_2O, 8.1%; CaO, 0.5%; Na_2O, 0.3%; and loss on ignition at 1050 °C, 11.35%. Alkali metal (Na and K) hydroxides and silica (cristobalite) were reagent grade chemicals supplied by Fluka.

The ash was submitted to the determination of particle size distribution by means of a Malvern Instruments Mastersizer 2000 laser analyser. The results are reported in Table 1.

The polycondensation reaction was carried out with different mixtures of the fly ash with alkali metal silicate solution of compositions stoichiometric to get geopolymeric products of the types PSS and PSDS. The alkali metal silicate solution was prepared by dissolving proper quantities of silica and sodium or potassium hydroxide in water. The amount of water used for the preparation of the alkali metal silicate solution was such to ensure constant workability of the mixes. Taking into account that the molar composition of the fly ash is $0.45(K_2O + Na_2O) \cdot Al_2O_3 \cdot 3.7SiO_2$, the stoichiometric amounts of alkali metal hydroxide and silica to be added to get the two different types of geopolymers were calculated as shown in Table 2.

Table 1
Coal fly ash particle size distribution

Size fraction (μm)	vol. %
<0.955	2.09
0.955–3.802	5.56
3.802–10.000	14.51
10.000–30.200	29.90
30.200–60.256	20.82
60.256–120.226	19.32
>120.266	7.80

Volume weighted mean diameter = 44.411 μm