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Research paper

Thermally treated clay sediments as geopolymer source material

C. Ferone [a],*, B. Liguori [b], I. Capasso [b], F. Colangelo [a], R. Cioffi [a], E. Cappelletto [c], R. Di Maggio [c]

[a] *Dipartimento di Ingegneria, Università Parthenope, Naples, Italy*
[b] *Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università Federico II, Naples, Italy*
[c] *Dipartimento di Ingegneria Civile, Ambientale e Meccanica, Università degli Studi di Trento, Trento, Italy*

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ABSTRACT

The management of reservoirs for water supply is a great environmental problem, since regular de-silting operations produce huge quantities of sediments. Among the recycling possibilities, the use of clay sediments for the manufacture of geopolymer-based materials seems to be an interesting alternative to disposal, due to their low cost and easy availability. In particular, two sediments, coming from reservoirs located in Southern Italy, were firstly characterized by X-ray diffraction, differential thermogravimetry, Fourier transformed infrared (FTIR) spectroscopy and ^{27}Al and ^{29}Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectroscopy. The reactivity of raw and thermally treated clay sediments in alkaline media was also investigated. Finally, geopolymeric samples were produced and chemically, physically and mechanically characterized. The results showed that the calcined clay sediments can be suitable source materials in polycondensation reactions and that the increase of the calcination temperature from 400 to 750 °C resulted in an increased reactivity. Moreover, good mechanical properties were obtained by all the geopolymers prepared with heat-treated sediments.

1. Introduction

The term “geopolymer” was coined by Davidovits in the 1970s, originally referring to the investigations on the reaction of metakaolin in alkaline media forming aluminosilicate polymers (Davidovits, 1976, 1999). The prefix “geo” was selected to symbolize the constitutive relationship of the binders to geological materials, natural stone and/or minerals. Their synthesis takes place by a process of polycondensation and can start from metakaolinite or many natural and artificial silicoaluminates by reaction with alkali metal (Na or K) hydroxide and/or silicate (Davidovits, 1991; Van Jaarsveld and Van Deventer, 1999; Cioffi et al., 2003; Andini et al., 2008; Ferone et al., 2011). In contact with a high pH alkaline solution, the starting materials dissolve, and geopolymer polycondensation takes place. Because of this reason, geopolymers are also considered as inorganic polymers based on aluminosilicates (Davidovits, 1993a). Amorphous geopolymers are obtained at temperatures from 20 to 90 °C, while crystalline ones are formed in autoclaves at temperatures up to 200 °C and autogenous pressures (Davidovits, 1991). Geopolymeric materials are attractive because of their excellent mechanical properties; durability and thermal stability can also be achieved (Palomo et al., 1992; Schmücker and MacKenzie, 2005). Owing to their low calcium content, they are more resistant to acid attack than materials based on Portland cement (Bakharev, 2005). In addition, they are of great interest because of the reduced energy requirement for their manufacture and the higher sustainability. In fact, the geopolymer technology has the potential to reduce emissions by 80% (Davidovits, 1993b) compared to that of Portland cement. Nowadays, eco-sustainability considerations suggest the use of waste from industrial processes as raw materials. The use of secondary resources such as fly ash and slags as aluminosilicate source material to form geopolymers has been widely proven (Palomo et al., 1999; Buchwald, 2006; Duxson et al., 2007). In particular, the use of fly ash promised high ecological benefit and lower cost, but may enclose difficulties in availability, handling or product quality (Winnefeld et al., 2010; Ferone et al., 2011). Recently the search for alternative low cost and easily available materials led among others to “normal clays”. Clay generally consists of a mixture of different clay minerals and associated minerals, which are strongly affected by the nature of the parent rocks (Brew and MacKenzie, 2007; Yip et al., 2008; Chen et al., 2009; Fonseca et al., 2010). These materials are widely available all over the world and may show certain reactivity after a thermal activation process (He et al., 1995a). In fact the thermal activation of clay minerals in the temperature range between 500 and 800 °C results generally in a dehydroxylation (Heller-Kallai, 2006), which causes the octahedral sheets lose water and decompose into a disordered metastable state (Evans and White, 1959; Mendelovici, 1997). This meta-state is widely addressed as being reactive as pozzolana (Ambroise et al., 1985, 1987;

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* Corresponding author at: Centro Direzionale, Is. C4-80143 Napoli, Italy. Tel.: +39 0815476713.
E-mail address: claudio.ferone@uniparthenope.it (C. Ferone).

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He et al., 1995a, 1995b, 2000; Baronio and Binda, 1997; Liebig and Althaus, 1997; Kakali et al., 2001; Sabir et al., 2001). Nevertheless, firing to higher temperatures results in the formation of new unreactive phases such as spinel and mullite (Mendelovici, 1997; Bondar et al., 2011a). Anyway, a careful calcination can activate the material leading to an increase of its geopolymeric reactivity (Xu and Van Deventer, 2002) and a consequent increase in terms of compression strength of the final product obtained. Among the silicoaluminate wastes, reservoir sediments are worthy of consideration. Most of these contain different types of clay minerals, mostly illite, smectite, chlorite and kaolinite, and must be periodically removed to avoid the progressive reduction in reservoir capacity. The management of reservoir sediments is a great problem, since regular de-silting operations can make huge quantities of sediments available. Among the recycling possibilities, applications as raw materials in the manufacture of artificial aggregate, bricks and cement clinker have recently been studied (Bernardo et al., 2000; Chiang et al., 2008; Liao and Huang, 2011a, 2011b; Tang et al., 2011). The use of clay sediments for the manufacture of geopolymer-based materials can be an interesting alternative to disposal (Chen et al., 2009; Ferone et al., 2013a; Molino et al., 2014).

The formation of geopolymers involves a chemical reaction between an aluminosilicate material and sodium silicate solution in a highly alkaline environment. The exact mechanism of geopolymerization is not yet fully understood, but it is believed to consist of three main stages: (1) the surface dissolution of Al and Si in a highly alkaline solution and diffusion of the dissolved species through the solution, (2) the polycondensation of the Al and Si complexes with the solution and the formation of a gel and (3) the hardening of the gel that results in the final geopolymeric product (Panagiotopoulou et al., 2007). The dissolution stage is the only one that can be quantitatively studied. For this reason, the leaching behavior of the calcined sediments in alkaline solution was investigated. A lot of papers have been published on the dissolution of aluminosilicate compounds, especially in the geochemical literature (Ganor and Lasaga, 1998; Köhler et al., 2003; Wolff-Boenisch et al., 2004; Criscenti et al., 2005). There are different solubility tests in alkaline solution that allow the direct determination of the amount of reactive silicate and aluminate species (Fraay, 1990; He et al., 1994, 1995a; Xu and van Deventer, 2000). Two of the main aspects of the test regime are the solution/solid ratio and the alkalinity of the solution used. In fact, too low values of the former (not enough dissolution) will result in condensation of the aluminosilicate. If this happens, the real amount of dissolved silicate and aluminate species cannot be measured in the solution.

The samples of clay sediments used in this work were collected from two different reservoirs for water supply, located in the south of Italy, Occhito (Carlantino, Foggia) and Sabetta (Morigerati, Salerno). Afterwards they were thermally activated at two different temperatures and then extensively characterized determining their chemical and physical properties in order to verify the behavior as source material for the preparation of geopolymer binders. Geopolymeric samples have been also produced and have been chemically, physically and mechanically characterized.

2. Experimental

2.1. Selection and characterization of the raw materials

Clay sediments were collected from two different reservoirs in the south of Italy: Occhito reservoir (Carlantino, Foggia), named throughout the text as OC, and Sabetta (Morigerati, Salerno), indicated as SA. Three cores were sampled from each lake. The cores were 10 cm in diameter and 1 m in height. The three cores coming from the same site were crushed in a jaw crusher, milled in a ring mill and carefully mixed to get a unique, homogeneous sample for each lake. After drying at 105 °C in an oven, the characterization of each sample was performed by means of chemical (quantitative), mineralogical, thermal and spectroscopic analyses. The chemical composition was determined by X-ray fluorescence, using a Bruker Explorer S4 apparatus. The mineralogical analysis was performed by means of a Philips PW 1730 diffractometer (Cu Kα radiation, 5–60° 2θ range, step width 0,02° 2θ; 0,02° 2θ/s scan speed; 0.5° slit width).

Semi-quantitative evaluation of the mineralogical phases was performed according to the following conditions: powders with grain size <10 μm were obtained by means of a McCrone micronizing mill (agate cylinders and wet grinding time = 15 min) and side loaded into the sample holder. An α-Al_2O_3 internal standard (1 μm, Buehler Micropolish) was added to each sample in the amount of 20 wt.%. Powder data set were obtained with a PANalytical X'Pert Pro modular diffractometer, equipped with a RTMS (Real Time Multiple Strips) detector (CuKα radiation, 40 kV, 40 mA, 2θ range from 3 to 80°, equivalent step size 0.0179° 2θ, equivalent counting time 120 s per step, 0.5° slit width). X'Pert High Score Plus 2.2d software and ICSD database were used for mineral identification and semi-quantitative evaluation.

Thermal analysis was performed using a Netzsch STA409PC Luxx apparatus (weight of the sample, 10 mg; heating rate, 10 °C min^{-1}; atmosphere, nitrogen and air).

The FTIR absorption spectra were recorded in the 4000–400 cm^{-1} range using a Nicolet system, Nexus model, equipped with a DTGS KBr (deuterated triglycine sulphate with potassium bromide windows) detector. A spectral resolution of 2 cm^{-1} was chosen. Each test sample (2.0 mg) was mixed with 200 mg of KBr in an agate mortar and then pressed into 200 mg pellets of 13 mm diameter. The spectrum of each sample represents an average of 32 scans.

Since the thermal activation can be useful for enhancing the sediment reactivity in polycondensation processes (Mendelovici, 1997; Buchwald et al., 2009), weighted amount of sediments were thermally treated at two different temperatures (400 °C and 750 °C for 2 h). The calcination was performed using a Nabertherm furnace with a heating rate of 10 °C/min. Blaine specific surface of each sediment, as received and heat treated, was measured according to UNI EN 196-6.

Sediments were also characterized by means of ^{29}Si MAS NMR analysis in order to investigate the modification of the structures after the treatments. The ^{29}Si NMR spectra were collected on a Bruker Avance 300 spectrometer ("Klaus Mueller Lab" of DII, University of Trento) operating at Larmor frequencies of 59.6 MHz. All the experiments were performed at room temperature and pressure, using air as spinning gas. The grinded samples were loaded in 7 mm zirconia rotors and spun at 4 kHz. The spectra were obtained using single-pulse RF excitation employing a pulse width of 5.5 μs and 5 s recycle delay to ensure quantitatively reliable spectra. Q_8M_8 was used as an external secondary reference.

The single pulse ^{27}Al NMR spectra were obtained on a dual channel Varian Infinity Plus 400 spectrometer (DCCI, University of Pisa) operating at Larmor frequencies of 104.24 MHz using a 3.2 mm T3-MAS HX probe.

For the ^{27}Al ($I = 5/2$) MAS-NMR signals, spectra were recorded after $\pi/6$ pulse irradiation (0.85 μs) and 1 s relaxation delay was used in order to excite only the central transition and ensure quantitative reliability. Samples were spun at 15 kHz and 6000 scans were collected. Chemical shifts were externally referenced to 1.0 M of $Al(NO_3)_3$ aqueous solution.

In order to verify the leaching in alkaline media of each raw material, before and after the thermal treatments, a reactivity test, able to evaluate the extent of dissolution of Si and Al in alkaline solutions, was used. The leaching of the raw materials was conducted by mixing 0.500 ± 0.001 g of solid with 20 ml of alkaline solution for certain time periods under continuous stirring. The variables studied were the concentration of the alkaline solution (3 and 7 M) and the time of dissolution (5, 10, 24 and 72 h). After filtering, the liquid part was diluted to 250 ml, the pH adjusted to pH < 1 by adding concentrated HCl acid (Panagiotopoulou et al., 2007) and plasma (Ar) optical emission spectroscopy (ICP-OES Perkin Helmer Mod. OPTIMA 2100 DV) was used in order to determine the Al and Si concentration.