



Alkali-activated calcined smectite clay blended with waste calcium carbonate as a low-carbon binder

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ARTICLE INFO

Article history:

Available online 24 February 2018

Keywords:

Alkali activation
Clay
Smectite
X-ray diffraction
X-ray tomography

ABSTRACT

Reconciling the need of producing reliable building materials, with that of drastically cutting greenhouse gas emissions represents one of the current fundamental technological and societal challenges. To this end, we assessed the performance of a binder alternative to ordinary Portland cement (OPC) based on the alkali activation of a blend of locally sampled, impure calcined clay of smectitic composition, with waste calcium carbonate from the marble industry.

The microstructure of the final product was investigated by means of scanning electron microscopy and X-ray tomography, and the phase composition by X-ray diffraction, implementing the POKKCS (partial or not known crystal structure) approach. Results of compressive strength tests show an adequate mechanical performance of these materials, with values of the compressive strength as high as 60 MPa after 20 days under room temperature curing. Replacement of a small quantity of the alkaline activator with sodium citrate induces enhanced workability and mechanical performance, reducing the amount of entrained air voids. The use of alkali activated calcined smectite clay – waste calcium carbonate blends represents a valuable complementary approach with respect to alkali activation of metakaolin and calcined kaolinite clay – OPC blends, towards the development of carbon-free binders.

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1. Introduction

Much effort and enthusiasm have been devoted, over the last few years, to the quest for new sustainable, environmental friendly, low-carbon binders, with the aim of designing the most viable solutions for cutting greenhouse gas emissions associated with the construction industry. To date, several reviews dealing with cleaner alternatives to ordinary Portland cement (OPC) have appeared in the literature (e.g. Flatt et al., 2012; Pacheco-Torgal et al., 2008; Palomo et al., 2014; Van Deventer et al., 2012).

Reconciling the needs of producing robust and reliable building materials and significantly cutting greenhouse gas emissions represents one of the current fundamental societal challenges, considering that: a) cement production contributes to 5–7% of the total anthropogenic CO₂ emissions (Barcelo et al., 2014) and b) the demand of houses and infrastructures is expected to rise, since 54% of the world population is currently living in urban areas. This figure is predicted to grow up to 66% by 2050, when the urban

population will grow by 2.5 billion people, 90% of which being concentrated in Africa and Asia (United Nations, 2014).

Two main research trends are being followed in order to provide an alternative to OPC. The first one is based on the production of blended cements, in which a given fraction of OPC is replaced by “supplementary cementing materials” (Siddique and Khan, 2011). Such materials comprise, among others, metakaolin, industrial by-products such as fly ash (from coal combustion) and ground granulated blast furnace slag (from steel production), or agricultural waste (such as rice husk ash). More recently, blends of OPC with up to 50% calcined low-grade clays (Scrivener and Favier, 2015) are being tested. This has the advantage of exploiting a raw material such as clay that, contrary to fly ash and slag, is abundant and promptly available worldwide (also in view of the fact that transport can play a relevant role in the overall impact, e.g. Peys et al., 2017), and cheaper compared to industrial high-grade metakaolin. The second option is based on the production of binders by alkali activation of materials such as metakaolin, slag and fly ash (Provis and van Deventer, 2014). Alkali activated binders are totally free of OPC and its embodied CO₂ deriving from limestone calcination. Nonetheless, the use of alkali activators (mostly sodium

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silicate and sodium hydroxide) results in an additional environmental cost, since their production has a non-negligible carbon footprint (Habert et al., 2011). The results of life cycle assessment (LCA) studies comparing the environmental performance of conventional cement and alkali activated binders are conflicting and a recent review estimates a global warming potential reduction for the latter of up to approximately 50% although the balance may even be negative for other impact categories such as water ecotoxicity and acidification (Ouellet-Plamondon and Habert, 2015). It has to be stressed, though, that the ecological footprint of alkali activators is possibly overestimated since LCA studies on this subject rely on not updated databases, based on processes of sodium silicate synthesis dating back to production year 1995 (Fawer et al., 1999) and such processes have reasonably become more efficient after more than 20 years.

In this study, we investigate the potential use of alternative binders based on alkali activated non-commercial, impure smectite clay. These clays are calcined and blended with calcium carbonate obtained as a by-product of the marble industry. Moderate CaCO_3 additions have been shown to improve the performance of alkali activated metakaolin (Yip et al., 2008; Cwirzen et al., 2014; Aboulayt et al., 2017). The clay was sampled in a not industrially exploited outcrop and possesses a different mineralogical composition compared to the low-grade clays normally used in OPC blends, which are mostly of kaolinitic composition (Antoni et al., 2012). Smectites are an important family of clay minerals forming from the alteration of volcanic glass, mostly in marine environment (Christidis, 2011). Only limited research on the performance of smectite or illite clays is present in the literature (Aldabsheh et al., 2015; Garg and Skibsted, 2014; Hu et al., 2017; Seiffarth et al., 2013). The additional use of waste calcium carbonate, an industrial by-product, adds environmental value to the material and reduces the consumption of primary raw materials, in line with the new paradigm of circular economy (Stahel, 2016), which meets the European Union agenda for waste minimisation and sustainable development (European Commission, 2015). This material, obtained in form of slurry during marble cutting, has been previously used as a filler in Portland cement (Aliabdo et al., 2014; Aruntas et al., 2010; Rana et al., 2015; Topcu et al., 2009) but, to the best of our knowledge, no use in combination with calcined clays appears in the literature. Finally, the effect of adding a small amount of sodium citrate to the activating solution was investigated. Sodium citrate can be used as a set retarder in OPC (Hewlett, 1998), although set acceleration, combined with improved workability and mechanical strength has also been observed (Wynn-Jones et al., 2014). Such opposite behaviours may depend on the amount of sodium citrate added, as it seems to be the case for citric acid (Singh et al., 1986). We found, during a previous investigation, that the addition of sodium citrate may drastically improve the mechanical strength of alkali activated fly ash (Reato, 2016). The use of potassium citrate has been reported to accelerate early hydration and retard later stages of the reaction kinetics of fly ash blended with OPC (Alahrache et al., 2016).

The performance of this alternative binder was investigated in detail, by assessing its microstructural development (by scanning electron microscopy and X-ray microtomography) and phase evolution (by X-ray diffraction) as well as mechanical strength of the hardened material.

2. Materials and methods

The smectite clay used in this study was sampled from an outcrop located in volcanic terrains in the Prealps (San Giovanni Ilarione, Verona, Northern Italy). Clays were calcined in a laboratory muffle for 3.5 h at a temperature of 750 °C, with a heating rate of

10 °C min⁻¹. This combination had shown to maximize mechanical strength during a preliminary investigation performed on commercial smectite clay. It has to be noted that the presence of Mg in the octahedral layer increases the dehydroxylation temperature to values close to those at which crystallization of new stable phases occurs (Emmerich, 2011), therefore it is necessary to tune the calcination temperature and time to obtain a trade-off between total clay structure decomposition and recrystallization.

The calcined clay was blended with waste calcium carbonate powder, obtained by oven drying a CaCO_3 slurry at 60 °C and grinding the dry residue. The slurry was a by-product of the marble industry, deriving from marble quarrying and cutting, which is still usually dumped and represents an environmental issue (Dino et al., 2017). Chemical (XRF) compositions of these materials are reported in Table 1. The clay phase composition as obtained by XRD (Fig. 1) consists mainly of smectite (66%) and of an amorphous component (22%), determined using a ZnO (zincite) internal standard, which can include a glassy phase and minor poorly-crystalline phases (e.g. oxides, hydroxides). Minor phases include calcite (4%), feldspar (3%), anatase (2%) and apatite (2%). The presence of a glassy phase is consistent with the volcanic origin of the material sampled in altered pyroclastic deposits. The XRD composition of the waste CaCO_3 powder consists of 100% calcite containing small Mg impurities. Particle size distributions obtained by laser diffraction are displayed in Fig. 2.

2.1. Binder preparation

Pastes were prepared by mixing 100 g of calcined clay with 50 g of activating solution for 5 min using a vertical stirrer. A second set of samples was prepared by replacing 25 g of clay with an equal amount of waste calcium carbonate powder.

The used activating solutions were synthesised from sodium hydroxide (NaOH) pellets and sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) powder. 50 g of solution contained 0.15 mol of Na_2O for the sodium hydroxide activator (38 g of deionized water) and 0.1 mol of Na_2O plus 0.1 mol of SiO_2 for the sodium silicate activator (27 g of deionized water). Moreover, the effect of replacing 5 g of the activating solution with 5 g of a sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) solution (0.03 mol of Na_2O per 50 g) was tested. After mixing, the pastes were poured in cylindrical polyethylene holders (having internal diameter and height of 2 cm and 3 cm, respectively) and kept in the sample holders for 24 h at 95% relative humidity. After the initial curing, the samples were dry-cured at room temperature (22 ± 2 °C) up to 20 days from mixing. The effect of water saturated curing was also tested by immersing the samples in tap water after being removed from the sample holders.

The samples used for the analyses are summarized in Table 2. A generic naming convention Xmn was used, where X indicates the type of alkali activator (S = sodium silicate; H = sodium hydroxide), m is a number indicating the presence (1) or absence (0) of waste calcium carbonate, n is a number indicating the presence (1) or absence (0) of sodium citrate.

2.2. Microstructural investigation

SEM-BSE microscopy of polished thin sections prepared from samples H11 and S11 was performed using a CamScan MX3000 (Applied Beams, Beaverton, US), equipped with an EDAX energy dispersive spectrometer, operated at 20 kV, with beam and aperture currents of 20 μA and 300 nA respectively, and 25 mm working distance.

X-ray microtomography (XCT) scans of samples S10 and S11 were performed using a Skyscan 1172 (Bruker, Billerica, US), with the aim of assessing the effect of sodium citrate on microstructural

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