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Research paper

Mix-design and characterization of alkali activated materials based on metakaolin and ladle slag

Maria Chiara Bignozzi [a,*], Stefania Manzi [a], Isabella Lancellotti [b], Elie Kamseu [b], Luisa Barbieri [b], Cristina Leonelli [b]

[a] *Dipartimento di Ingegneria Civile, Ambientale e dei Materiali, Università di Bologna, Via Terracini 28, 40131 Bologna, Italy*
[b] *Dipartimento di Ingegneria dei Materiali e dell'Ambiente, Università di Modena e Reggio Emilia, Via Vignolese, 905/a, 41100 Modena, Italy*

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ABSTRACT

Recycling industrial waste to produce new materials is a driving path to promote a sustainable development. Alkali activation can be a very effective tool to reach this goal especially when the starting material can be carbon fly ash and blast furnace slag instead of calcined natural clays such as metakaolin. With the aim to further increase the type of waste to be used as precursor and to promote a new recycling route, alkali activated materials based on partial substitution of metakaolin with ladle slag, deriving from the refining process of steel produced by arc electric furnace technology, are reported. In particular, being ladle slag rich in Ca-containing crystalline phases, its effect on the consolidation process has been investigated by means of microstructure analysis carried out with XRD, SEM and MIP techniques. The results show that ladle slag are activated by alkaline solutions and participate in gels formation. Indeed, an optimization in terms of ladle slag content (60–80 wt.%) and the coexistence of different types of gels (3D aluminosilicate, C-S-H and Ca-rich aluminosilicate) have been envisaged.

1. Introduction

Alkali activated materials have been shown to offer an environment friendly and technically competitive alternative to ordinary Portland cement (OPC), and are increasingly being employed in various applications (Davidovits, 2008; Duxson et al., 2005, 2007a; Komnitsas and Zaharaki, 2007; Yip et al., 2008).

Metakaolin has been largely investigated as a geopolymer precursor (Davidovits, 1984, 1991, 2008; Duxson et al., 2005; Xu and van Deventer, 2000). In terms of chemical composition, the main difference between geopolymer based on metakaolin and OPC is the presence of calcium in the reaction products. Indeed, geopolymers are characterized by a binding phase which is almost exclusively aluminosilicate and highly coordinated (Q^3 and Q^4 where Q^n indicates $(SiO_4)^{4-}$ tetrahedra with n bridging oxygens). Calcium can be present, but it does not take part in the consolidation process. Inorganic polymers (IP) and alkali activated materials (AAM) are terms that are largely applied today to materials obtained by precursors based on both aluminosilicate and Ca-containing amorphous or crystalline phases. AAM includes all the binder systems derived by the reaction of an alkaline salt (alkali hydroxide, silicates, carbonates, etc.) with a solid silicate powder (Pachego-Torgal et al., 2008). The solid silicate can be based on calcium (e.g. clinker) or aluminium (e.g. metallurgical slag, pozzolan, etc.). IPs are included in AAMs, but in this case the primary binding phase is a disordered silicate network and a minor content of calcium, compared to AAM, which promotes the formation of highly crosslinked structures where Q^3 and Q^4 are more prevalent (Shi et al., 2006; van Deventer et al., 2010).

Metakaolin is obtained by calcination of natural kaolin, usually at 700 °C, thus requiring energy for its production (Elimbi et al., 2011). With the goal to save natural raw materials as well as to promote energy saving processes, IP and AAM systems based on industrial waste such as carbon fly ash (Fernández-Jiménez et al., 2005; Izquierdo et al., 2009; Guo et al., 2010; Temuujin et al., 2009) and blast furnace slag (Bernal et al., 2011; Oh et al., 2010) have been recently developed. The introduction of waste, rich not only in silica and alumina, but also in different monovalent and divalent metal oxides, has driven the research towards specific investigations on the effects promoted by the presence of different chemical and mineralogical phases in the precursors. However, as carbon fly ash and blast furnace slag are successfully employed as pozzolan and blast furnace cements, their use for alkali activation process could be rather limited in Europe, where an effective recycling route in cement industry is well assessed.

As recycling further industrial waste to produce new AAMs is a challenging issue towards reduction of landfill disposal and safeguard of not renewable raw materials (Lancellotti et al., 2010), this work aims at investigating the possible use of electric arc furnace slag as a precursor for alkali activation process.

Electric arc furnace slag comes from the ladle (ladle slag, LS) where the refining process of steel produced by arc electric furnace technology occurs (Crompton, 2001). Ladle slag accounts for about 1/3 of the total

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[*] Corresponding author. Tel.: +39 0512090342; fax: +39 0512090322.
E-mail address: maria.bignozzi@unibo.it (M.C. Bignozzi).

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amount of slag usually produced in electric arc furnaces and its European production can be estimated about 4 millions t/year (Kourounis et al., 2007). At present, this slag is generally treated as waste and dumped in landfills. Beside aluminosilicate, ladle slag contains calcium–silicate and calcium–aluminate, thus introducing phases that are not usually involved in metakaolin consolidation process.

In the current study, mix design, microstructure, as well as physical–mechanical characterization of the new systems based on metakaolin and ladle slag in different amount are reported and discussed with the goal to highlight the effects of ladle slag addition on the activation and consolidation process. The presence of calcium based crystalline phases in the slag represents a challenge since their soluble/reactive portion could take part and positively contribute to the synthesis of the final products. So far these aspects have only been marginally investigated for this kind of slag (Bignozzi et al., 2010; Natali et al., 2011), whereas several detailed studies have been addressed to blast furnaces slag, containing CaO and SiO_2 in the range of 36–42 and 35–39%, respectively (Bernal et al., 2011; Lecomte et al., 2006; Oh et al., 2010; Pal et al., 2003). Indeed, the joint activation of metakaolin and ladle slag allows the activation process to occur at room temperature, thus favouring an additional energy saving compared to metakaolin geopolymeric systems often requiring 70–80 °C as curing temperature.

Finally, the findings of this study are fundamental to further investigate on the durability aspects and final applications of alkali activated system based on metakaolin and ladle slag.

2. Experimental

2.1. Materials

Metakaolin (MK) was obtained by calcining commercial kaolin (Argirec B24, AGS Mineraux, Clerac, France) at 700 °C for 5 h. MK has 50% (D_{50}) and 95% (D_{95}) passing at 6 μm and 30 μm sieves, respectively. Mineralogical analysis of MK shows minor crystalline impurities identified as (K, Na) (Al, Mg, Fe)$_2$ ($Si_{3.1}Al_{0.9}$) O_{10} $(OH)_2$ Muscovite-3T (ICDD #07-0042).

Ladle slag was kindly supplied by Acciaieria di Rubiera SpA, Casalgrande, RE, Italy. A highly representative sample was directly collected in the steel productive plant. The slag is usually piled in a covered area of the industrial plant, waiting for landfill disposal that usually occurs every 2–3 months. The slag, collected from the refining process that occurs in transport ladles of the steelmaking plant, has a fine size since its production, however the fraction >0.105 mm was eliminated by sieving with the purpose to obtain a grain size distribution smaller than 0.1 mm. The sample, with 50% (D_{50}) and 95% (D_{95}) passing at 27 μm and 90 μm sieves, respectively, has been named LS. Scanning electron microscopy images of MK and LS are reported in Fig. 1. The difference between MK and LS particle sizes are clearly evident as well as the angular shape of LS particles.

Mineralogical analysis of LS shows many crystalline phases identified as follows: calcium–silicates, calcium–aluminates and calcium–aluminium–silicates as $\gamma{-}C_2S$ Ca_2SiO_4 Olivine (ICDD # 180–941), $Ca_2(Al(AlSi)O_7)$ Gehlenite (ICDD #174–1607), $Ca_{12}Al_{14}O_{33}$ Mayenite, syn (ICDD #170-2144) and iron-magnesium-calcium-silicate. Periclase MgO (ICDD #45–0946) and traces of Oldhamite CaS (ICDD #38–1420), coming from the desulfuration process, $\beta{-}C_2S$ Ca_2SiO_4, $Ca(OH)_2$, calcium and magnesium carbonates, have also been determined (Bignozzi et al., 2010). Due to the high content of different crystalline phases, a quantitative determination of amorphous phase in LS is very difficult. The lack of quantitative data for amorphous phase content in steel slag, thus proving the difficulty in the evaluation, is confirmed by the literature (Frias Rojas and Sánchez de Rojas, 2004; Kourounis et al., 2007; Shi, 2002), however average values of 20% and 35 ± 5% have been recently reported for stainless steel ladle slag (Kriskova et al., 2012) and ladle slag much richer in aluminium oxide than LS (Adolfsson et al., 2011), respectively.

Chemical analyses of LS and MK were carried out by X-Ray fluorescence spectrometer (XRF, PW 1414, Philips Thermo ARL (ADVANT'XP+)) for the main oxides and the relevant data are reported in Table 1. According to its origin, LS shows a high content of CaO (54.5%) and a certain amount of MgO (4.0%), besides SiO_2, Al_2O_3 and Fe_2O_3. As expected, MK is mainly constituted by SiO_2 (53.6%) and Al_2O_3 (41.7%), and small content of others elements such as Fe_2O_3 and TiO_2.

The tendency of LS to dissolve in alkaline environment was tested mixing 20 g of LS in 100 ml of 8M NaOH solution under stirring for 12 h. The residue was filtered and analyzed by X-rays.

Sodium silicate ($SiO_2/Na_2O = 1.99$, density at 20 °C $= 1.51 \pm 0.20$ g/cm^3, viscosity at 20 °C $= 250 \pm 150$ mPa·s — Ingessil, Verona, Italy) and 8 M NaOH were used as activating solutions.

2.2. Samples preparation

MK and/or LS were mixed in a planetary mixer according to the formulations reported in Table 2. Each mix was named with prefix G (for geopolymer), followed by MK content, with the exception of the sample containing 100% LS (G-LS100).

After 10 min of mixing, sodium hydroxide and sodium silicate solutions in a 1:1 weight ratio were added forming homogenous slurry. When necessary, distilled water was also added to improve the slurry workability. After 5 min of mixing, the slurry was transferred in moulds

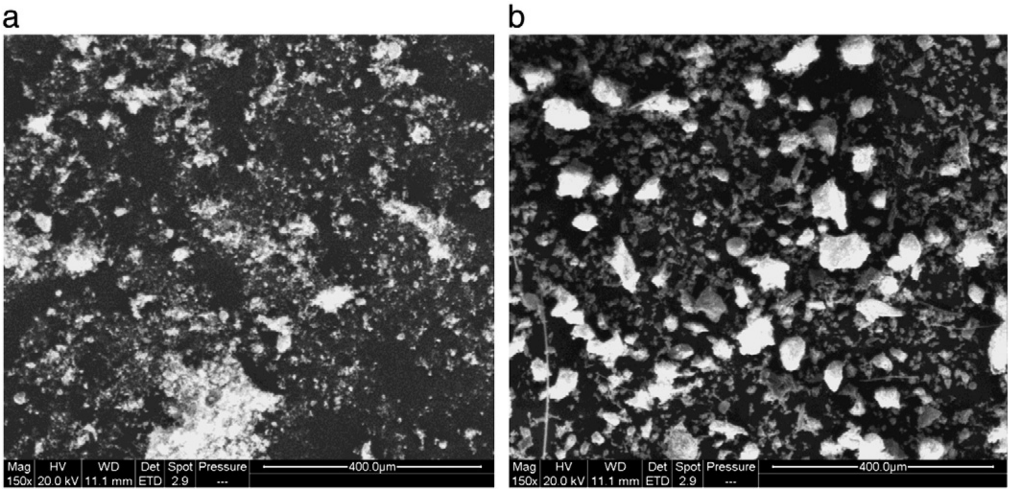

Fig. 1. SEM images of metakaolin (a) and ladle slag (b) particles.