Synthesis and characterization of geopolymers containing blends of unprocessed steel slag and metakaolin: The role of slag particle size

E. Furlani*, S. Maschio, M. Magnan, E. Aneggi, F. Andreatta, M. Lekka, A. Lanzutti, L. Fedrizzi

University of Udine, Polytechnic Department of Engineering and Architecture, Via Del Cotonificio 108, 33100 Udine, Italy

A B S T R A C T

The present research deals with the production and characterization of geopolymers prepared by mixing metakaolin with a steel slag from the production of chromium-manganese steel, a commercial sodium silicate solution and a sodium hydroxide solution. Different specimens were prepared by mixing metakaolin with different proportions of steel slag (20, 40, 60, 80 wt%) characterized by different maximum particle size. Specimens containing just metakaolin and steel slag alone were also prepared for comparison. All specimens have been characterized regarding their compressive strength, specific surface area, water absorption and microstructure. It has been observed that the use of fine steel slag powders leads to increases the performances and that the specimens containing 40 wt% steel slag and 60 wt% metakaolin revealed the best overall behaviour.

1. Introduction

Following the approach that was originally proposed by Davidovits [1–3], many other researchers have contributed to enrich the literature and knowledge regarding geopolymers and geopolymer based materials. Most of the works regard the preparation conditions and chemical reactions which take place during the formation of the geopolymer and its curing [4–16]. It is generally accepted that the addition of an alkaline solution is necessary to improve the pH of the geopolymeric paste during the initial stage of the polymerization [17–22]. It was also shown that the presence of a silicate solution could balance the Si/Al atomic ratio inside the geopolymeric paste leading to the formation of homogeneous interconnected structures which are necessary to develop good mechanical performances [23–25]. On the other hand, a thermal treatment, at moderate temperature, after casting the gel slip, could accelerate/improve the consolidation of the suspension [26–30]. Results reported in literature prove that geopolymers could be obtained starting from high grade synthetic components [31–39], but also by the reaction between recycled products such as fly ashes [40–48], granulated blast furnace slag or steel slag [49–57], red mud [58,59] and alkaline compounds.

The use of waste granulated blast furnace slag (GBFS) or steel slag (SS) is also widely documented in literature as component for mortars or concrete production [60–69]. In this subject area, several authors proposed to recycle SS or GBFS as a material for a partial replace of cements [70–74] and many others suggested its use as partial or total replacement compound for aggregate [75–79]. In both cases the resulting materials, i.e. hardened mortars or concretes, display good durability and mechanical performances that are suitable for civil engineering applications.

However, due to the huge quantity of SS or GBFS produced all over the world (any ton of steel implies the production 150–200 kg of SS or GBFS) any other possible way for recycling is well accepted and the production of geopolymers follows this approach. The present paper investigates geopolymers obtained mixing SS, metakaolin, a sodium silicate solution and sodium hydroxide solution (activator). In this work the sodium silicate solution was employed to obtain a Si/Al atomic ratio as close as possible to 1.9 while maintaining the Al_2O_3/Na_2O molar ratio around 1. In parallel, a SS free set of samples was also studied as reference composition, in order to evaluate the effect of SS on the properties of the geopolymers

2. Experimental procedures

2.1. Starting materials

The starting materials used for the geopolymer-slag composites synthesis were: a natural kaolin (Kaolin HIII GF, Dorfner GmbH, Hirschau, Germany), received as a powdered product industrially used for the production of tiles, a steel slag, obtained from the production of a chromium-manganese austenitic steel by a rotary kiln, a commercial sodium silicate solution, containing 50% wt of water with 2.84 wt SiO_2/Na_2O ratio (2.94 M), and sodium hydroxide pellets 98% (Titolchimica Spa-Pontecchio Polesine, Ro-IT). The chemical

Table 1
Composition, LOI and density of Kaolin and SS. "Others" indicates the cumulative quantity of all oxides determined in quantity lower than 0.1 wt%.

Component	Kaolin (wt%)	SS (wt%)
CaO	0.05	38.9
SiO_2	49.2	15.0
Al_2O_3	36.0	6.7
MgO	0.09	11.6
Na_2O	0.08	–
K_2O	1.1	–
Fe_2O_3	0.34	10.2
MnO	–	11.3
Cr_2O_3	–	1.8
V_2O_5	–	0.6
P_2O_5	0.28	0.9
TiO_2	0.31	–
Others	0.25	2.85
Free Lime[a]	–	1.7
LOI (%)	12.3	0.15
Density (g/cm^3)	2.59	3.30

[a] The amount of free CaO was measured, in a second time, following the ethylene glycol method.

compositions of kaolin and as received steel slag are reported in Table 1 together with their lost on ignition (LOI) and density. The chemical analysis was obtained by a Spectro Mass 2000 Induced Coupled Plasma (ICP) mass spectrometer, whereas LOI was determined after a thermal treatment at 1000 °C for 2 h. The amount of free lime in the slag was determined following the ethylene glycol method whereas densities were determined following the ASTM C127 and C128 standards.

2.2. Preparation and characterization of the starting materials

The as received granulated slag was used without any previous wetting, weathering or other ageing treatments. It was dry milled by a hammer mill in order to reduce its maximum particle size below 5 mm. The milled product was used for the preparation of two separated batches of powders having different maximum particle size: 250 μm (SS250) and 125 μm (SS125), respectively. Each batch of powder was used alone or blended with metakaolin as starting component for the preparation of a set of geopolymeric samples.

The starting crystalline natural kaolin was transformed into a quite amorphous powder by thermal treatment at 750 °C for 3 h and cooled following the natural cooling trend of the furnace.

Sodium hydroxide pellets were used to prepare an 8 M solution by a dissolving the required amount of solid NaOH in distilled water. After preparation, the solution was stored for 24 h at room temperature in a closed glass container.

The mix proportion design, referred to 100 g of powdered material, is reported in Table 2 together with the samples denomination used hereafter. The variability of Al_2O_3/Na_2O and H_2O/Na_2O ratios with materials composition, takes account of the different phase composition

of the two SS powders used for the preparation.

The particle size distribution (PSD) of kaolin, metakaolin and the two selected batches of steel slag were determined by a Horiba LA950 laser scattering particle size analyzer. Analyses were made in water after 3 min sonication. PSD curves (cumulative representation) are displayed with logarithmic abscissa.

The crystalline phases of slag and metakaolin were investigated by X-ray diffraction (XRD). XRD patterns were acquired by a Philips X'Pert diffractometer operating at 40 kV and 40 mA using Ni-filtered Cu-Kα radiation beam. Spectra were collected using a step size of 0.02° with a counting time of 40 s per angular abscissa in the range of 10–80°. The Philips X'Pert HighScore software was used for phase identification whereas their semi-quantitative evaluation was obtained following the RIR method [80].

2.3. Samples preparation

Geopolymer samples were prepared, following the mix proportion reported in Table 2, by mechanically mixing metakaolin, steel slag, sodium silicate and hydroxide solutions. Mechanical mixing was performed by a Hobart stirrer (5 L capacity). After 30 min of mixing, slurries were poured into high density cylindrical nylon moulds, vibrated for 2 min to remove air and sealed by a plastic film. It has been observed that, during the first stage of homogenization, slurries presented high viscosity which progressively decreased on working so that slips could be easily poured into the moulds at the end of the mixing process.

Spread-flow test was carried out in order to evaluate workability of the slurries [81,82]. In the present research slurries were poured into a truncated conical mould (top diameter = 70 mm, bottom diameter = 100 mm, height = 60 mm), which was filled up to the top; after 1 min, the conical mould was lifted vertically and the diameter of the paste after spreading was measured along two perpendicular directions. The relative slump value was derived from the following equation:

$$K = (d/d_0)^2 - 1$$

where K is the relative slump, d is the diameter of the cake spread and d_0 the bottom diameter of the conical cone; K_0 is the value calculated on the control composition.

After preparation, the slurries were aged into the moulds at room temperature for 24 h and then cured at 60 °C under environmental pressure for further 24 h. Successively, they were removed from the moulds, sealed again by a plastic film and maintained at room temperature and pressure for 28 days before being used for characterization and testing.

2.4. Characterization of hardened materials

Compression tests were performed on cylindrical specimens with 60 mm diameter and 120 mm height (in accordance with the ASTM C39 standard), using an 810 Material Test System with a crosshead speed of

Table 2
Mix proportion design of the compositions prepared referred to 100 g of powdered material.

Sample name	Metakaolinite (g)	Slag < 125 μm (g)	Slag < 250 μm (g)	Sodium silicate solution (g)	Na hydroxide solution (g)	Si/Al	Al_2O_3/Na_2O	H_2O/Na_2O
M	100	0	0	90	40	1.94	1.01	11.5
MS20-1	80	20	0	90	30	1.94	1.03	11.7
MS40-1	60	40	0	91	25	1.94	0.99	12.0
MS60-1	40	60	0	91	20	1.94	0.93	12.2
MS80-1	20	80	0	91	20	1.94	0.80	12.2
S1	0	100	0	91	15	1.94	0.73	12.4
MS20-2	80	0	20	92	30	1.94	1.03	11.8
MS40-2	60	0	40	96	25	1.94	0.95	11.7
MS60–2	40	0	60	99	20	1.94	0.91	12.2
MS80-2	20	0	80	101	20	1.94	0.80	12.2
S2	0	0	100	105	15	1.94	0.71	12.4