Effect of curing temperatures on the alkali activation of crystalline continuous casting stainless steel slag

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HIGHLIGHTS

- Continuous casting slag shows hardening with alkali silicates under steam curing.
- Strength improvement is initially gradual but steeper at higher temperatures.
- Short term strength is dependent on alkali cations.
- Porosity of the mortars is more affected by alkali cations than curing temperature.
- Bonding between aggregate and matrix is majorly affected by curing temperature.

ARTICLE INFO

ABSTRACT

The binding properties of continuous casting stainless steel slag were studied when activated by a combination of Na silicate and 5 M NaOH as well as K silicate and 5 M KOH at steam curing temperatures of 60, 70, 80, 90, 100 and 110 °C. The slag mortars developed moderate compressive strength ($\sim$5 MPa) at 60 °C which initially increased moderately and then steeply (>30 MPa) at higher curing temperatures. The porosity of K activated mortars was lower than for Na activated mortars. Thermal and ATR-FTIR analysis showed the formation of C–S–H type of reaction products for both activators at all temperatures, while the formation of brucite was promoted at higher curing temperatures. A much denser hydrated matrix with a better bonding with aggregates was formed at higher curing temperatures. Heavy metal leaching from the slag was dependent on its type and curing temperature of samples.

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1. Introduction

The credibility of alkali activated materials and their being a competitive alternative to ordinary Portland cement (OPC) has been proved since long [1,2] and it has been fairly well reconfirmed by several recent publications [3–5]. Most of these works concentrate on ground granulated blast furnace slag (GGBFS), which is a highly vitreous material, and it has been recognized that it is a material with immense potential to act as a binder. Recently the focus has shifted to several other slags coming from steel and stainless steel processing, which although produced in lower amounts compared to GGBFS, are still available in substantial quantities [6,7]. The chemical composition of these slags place them fairly close to that of OPC and GGBFS, and hence suggest possible potential to act as binders. The major difference, however, lies in the phase composition. While the GGBFS is mostly glassy, the steel and stainless steel slags, due to their higher basicity (CaO/SiO_2), are highly crystalline in nature and whereas the crystalline phases in OPC are mostly hydraulic, the ones present in stainless steel slags are mostly considered non-hydraulic [8]. Therefore, modifications in the treatment are required in order to generate binding properties in these slags.

Continuous casting (CtCs) slag is produced at the final stage of stainless steel processing. This slag stands out because of its typical dusty appearance which is due to the presence of large amounts of dicalcium silicate (C_2S) which undergoes polymorphic transformations during cooling. The most important one is the β → γ

transformation that occurs around 500 °C and is accompanied by a volumetric expansion of ~12% [9]. This phenomenon results in pulverisation of the slag into fine powder, a process called dusting. Although dusting is a serious problem for the industry as it causes difficulties in the handling as well as in the valorisation of this slag, it has an inherent advantage for use as binder as it foregoes the energy and cost intensive milling process. It is possible therefore that simpler and less energy intensive methods, like sieving, can be used to separate the material to be valorised.

Although few in number, some publications regarding the investigation of hydraulic properties of crystalline slags do exist in literatures [6,10–12]. In most of these studies the activation of binding properties in the slag was achieved by mixing with other materials like OPC or GGBFS or by mechanical activation. The authors of the present work also found that if CtCs slag is activated solely with alkalis, high temperature curing (via steam curing) is required for the initiation of hardening reactions which are not initiated in the slag even after prolonged curing at room temperatures [7]. Although the proof of concept regarding the binding potential of CtCs slag was established in this previous study, the behaviour at different curing temperatures and the ultimate potential of this slag as a binder still remains unexplored. Such investigations shall be beneficial for deciding the suitable application for the valorisation of this material. Within this context, the current research is aimed at investigating the effect of different steam curing temperatures on the mechanical strength development, hydraulic properties, porosity, microstructure and leaching behaviour of CtCs slag activated using Na and K alkali solutions.

2. Materials and methods

2.1. Materials and sample preparation

The CtCs slag was obtained from a Belgian stainless steel plant. The slag was sieved and the fraction finer than 80 μm (CtCs_80) was used for the current work. This fraction consists of approximately 60 wt.% of the total slag. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) solutions of 5 M were prepared by mixing the respective pellets in distilled water. These solutions were prepared at least 24 h before using them. The 5 M NaOH was mixed with commercially available sodium silicate (ABCR GmbH & Co. KG, 39–40% silicates in water) solution and the 5 M KOH was mixed with commercially available potassium silicate (R&D Lab. Ltd., weight ratio 1.40:1–1.45:1, total alkali as K_2O 21.1–22.1%) solution in 50:50 weight ratio to give a resulting modulus (molar ratio of SiO_2 and alkali oxide) of 1.4 for both mixes. These mixtures were used as activating solutions.

Mortar samples were prepared using CtCs_80 slag and 0–5 mm river sand was used as aggregate. Slag to aggregate weight ratio was kept at 1:3 and activator to slag weight ratio at 0.7. The actual water to slag ratio with Na activator was 0.65 and with K activator was 0.60. The mixing was performed in accordance with EN 196-1 [17]. The mortar was cast in the form of $4 \times 4 \times 16$ cm^3 beams in steel moulds and the compaction, to remove air bubbles, was carried out in a jolting machine conforming to EN 196-1. Elevated temperature curing was provided in a steam curing chamber. Six different steam curing temperatures starting from 60 °C to 110 °C at an increment of 10 °C were used. The highest temperature was limited to 110 °C as temperature increase beyond this required an increase in pressure in the steam curing chamber above atmospheric conditions. The steam curing cycle involved a pre-steaming/delay period of 3 h in ambient laboratory conditions (20 °C, 60% RH), followed by curing in a steam curing chamber at different temperatures for 16 h and cooling for 5 h. The total steam curing cycle, thus, was 24 h. The samples were then cured in a moist room (20 °C, >90% RH). Mortar samples were taken at 3, 7, 28 and 90 days for compressive strength measurements. Samples of slag pastes (CtCs_80 and activating solution) were also prepared following the same curing cycle for analysis.

2.2. Analysis and testing

The particle size distribution of the slag was determined by wet laser diffraction (Malvern Mastersizer). The slag sample was mixed in ethanol to prevent any possible hydration. The test was done in triplicate over the sample.

The chemical composition of the slag was determined by X-ray Fluorescence (XRF) spectrometry using a Philips (PW 2400) automatic sequential wavelength dispersive XRF spectrometer and quantified using the SuperQ software.

Quantitative X-ray diffraction (QXRD) data were collected using a Philips Analytical PW 1710 diffractometer with Cu Kα radiation (λ = 1.54 Å) operating at 45 kV and 35 mA. The samples were scanned over a range of 10–70° 2θ, measured in step

scan mode at 2 s per 0.02° 2θ. A 10 wt.% ZnO internal standard was added to the samples to determine the amorphous phase content. Phase identification was carried out using DiffracPlus EVA software. Topas Academic v4.1 [13] software was used for Rietveld quantitative phase analysis.

The particle density of the slag was determined by pycnometer analysis as per EN 1097-6 [14] and the specific surface area was determined by the Blaine method [15].

Thermogravimetic analysis (TGA) was carried out using a Netzsch STA 409 PC DSC-TGA equipment in a through flow N_2 atmosphere (60 ml/min) over a temperature range of 20–1000 °C at a controlled heating rate of 10 °C/min. The first derivative of thermogravimetry (DTG) was used in order to identify the reaction products.

Attenuated total reflection Fourier transform-infrared (ATR-FTIR) spectra were recorded on a Perkin Elmer Frontier spectrometer in the region of 4000–650 cm^{-1} at a resolution of 1 cm^{-1}.

The samples of slag pastes for TGA and ATR-FTIR were powdered and vacuum dried at 0.023 mbar for 2 h in order to stop the hydration reactions. Under such vacuum drying conditions any moisture or free water in the sample is completely removed and the only water available in the sample would be bound water [16]. The samples were then stored in vacuum desiccators until analysis.

Open porosity of the activated slag mortars was determined by the water saturation test by hydrostatical weighing as per EN 1936. The pore size distribution of the samples was determined using Mercury Intrusion Porosimetry (MIP, Micromeritics AutoPore IV 9500). The instrument was composed of a low (3 bar) and a high (until 2000 bar) pressure unit. The contact angle of the Hg was set to 130°.

The microstructural investigation of the activated slag was done by SEM analysis (Phillips XL30) on fractured slag paste samples after 90 days of hydration in the secondary electron mode. For the microchemical analysis, wavelength dispersive spectroscopy (WDS) was employed by means of a field emission microprobe (JXA-8530 F, JEOL). The analyses were performed on polished mortar samples after 90 days of hydration.

Batch leaching tests were performed, in triplicates, on fresh and activated samples to determine the effect of alkali-activation and steam curing temperatures on the mobility of regulated metals and on the material basicity according to standard procedure EN 12457-4/DIN 38414-S4. For each sample, an amount of 10 grams of solids was mixed with 100 ml ultrapure (18.2 MΩ cm) water (L/S = 10) in a sealed PE bottle, and shaken on a vibration table (Gerhardt Laboshake) at 160 rpm at 25 °C for 24 h. Determination of aqueous elemental concentrations was performed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Thermo Electron X Series). The leaching solutions were diluted 20× for ICP-MS measurement; the solution matrix was 0.3 M nitric acid. The slag samples for leaching were the same as the ones used in the TGA and FTIR analysis.

3. Results and discussion

3.1. Characterisation of the slag

The particle morphologies of the slag are shown in Fig. 1. The angular morphology of the particles and the variations of the sizes are apparent from the figure. The particle size distribution of the slag is shown in Fig. 2. The cumulative plot (inset Fig. 2) shows that 80 vol.% of the particles are less than 59 μm. The d$_{50}$ of the slag was found to be 35.5 ± 0.2 μm. Approximately 7 vol.% of particles that appear larger than 80 μm in the laser diffraction is due to the fact that sieving is essentially based on a selection of a minimal particle diameter that enables the particles to pass the sieve. Since the particles of the slag are not always spherical, as is apparent from Fig 1, the mean dimension, as determined by laser diffraction, can be higher.

The oxide composition of the slag determined by XRF analysis is displayed in Table 1. CaO forms the largest constituent in the slag. It comes as a result of lime additions during the processing of the molten metal. Silica is the second oxide in abundance. It is typically formed as a result of deoxidation of the steel due to reaction between oxygen and silicon dissolved in the steel. In stainless steel Si is also added to the melt to protect the Cr from oxidation. A substantial content of MgO can also be observed in the composition. It comes as a result of dolomite additions as flux and from the refractory linings of the furnace. The other oxides are present in much smaller quantities. The value of Cr reported is reported in terms of oxide. The actual Cr content is 0.86 wt.%.

The phase composition of the slag in Table 2 (XRD pattern in Fig. S1 of the supplementary content) shows that γ-C_2S is the