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Calcium aluminate rich secondary stainless steel slag as a supplementary cementitious material

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HIGHLIGHTS

- Characterization of slag derived from stainless steelmaking refining processes.
- Secondary stainless steel slag contain hydraulic phases, predominantly calcium aluminates.
- Study of cement composites in which cement is replaced by secondary stainless steel slag.
- Investigation of strength development, hydration products, and porosity.
- Secondary stainless steel slag is a promising supplementary cementitious material.

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ABSTRACT

Detailed characterization of calcium aluminate rich secondary steel slag derived from two different refining processes of stainless steel production has been performed in order to gain generic knowledge about this by-product, and its behaviour as a supplementary cementitious material. Additionally, slag blended cement composites were investigated and compared to a limestone filler blended cement composites and to a reference cement composites. The results showed that the investigated slag contained several hydraulic phases, mainly in the form of calcium aluminates. In the case of the slag cement composites, a larger proportion of hydration products was observed than in the case of the limestone cement composites, as well as a higher rate of strength increase.

1. Introduction

A transition towards a resource-efficient, low-carbon, closed-loop based economy is vitally needed by our planet. In view of the large scale occurrence of waste and industrial by-products, the challenge lies in the development of integrated zero-waste flow sheets, in which these materials are recovered and incorporated into new products, among which construction materials are particularly important [1]. Such a “green building” approach presents an opportunity for sustainable growth in the building and construction industry, which is strongly supported by the Construction Products Regulation No. 305/2011 [2], and includes the additional Basic Requirements No. 7, where the use of environmentally compatible raw materials in construction works, as well as secondary materials is required. Also, the Waste Framework Directive 2008/98/ES [3] has prescribed a new waste management hierarchy, where priority is given to reuse and recycling. However, waste and by-products from industrial production can only be used when the final construction composites obtained have appropriate functional properties, and do not present an environmental hazard [4].

Among the most promising industrial waste or by-products for recycling and application in the construction industry are different types of steel slag. The amount of steel slag produced in Europe was, in 2010, about 21.8 million tonnes [5]. A large part of this slag is re-used and recycled, mainly in road construction. However, some types of slag have a low potential for recycling. These are secondary (refining) metallurgical slags from ferrous production, of which approximately 2.8 million tons were disposed of in 2010 [5]. In comparison with other types of steel slag (e.g. EAF C slag), secondary slags generally have a highly variable mineralogical

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composition, and a high content of free CaO and MgO due to the effect of several different factors, e.g. the variety of the metallurgical processes, batch synthesis, and scrap metal variations [6–9]. Furthermore, the manner of handling of the slag at slag yards must also be taken into account [6]. This means that the potential re-use of every type of secondary steel slag has to be considered separately, in its own case study.

Despite the shortcomings associated with secondary metallurgical slags, various studies have discussed its potential usage in the construction and civil engineering applications [10,11]. The results of researches have shown that secondary metallurgical slags could be successfully incorporated in useful mixtures for the construction industry [7,8,12–14]. The use of secondary steel slag in the production of cement composites has been studied as an aggregate substitute [8,12,15–17], as a filler material [14], and, since secondary metallurgical slags may possess hydraulic and/or latent hydraulic (pozzolanic) characteristics, also as a supplementary cementitious material (SCM) [6,7,9,12,13,18–20]. In order to improve the characteristics of cement composites into which secondary metallurgical slags have been blended, such slag was pre-treated in the laboratory (i.e. by artificial weathering, grinding, sieving, magnetic separation, and enhanced carbonization) before being incorporated in cement composites, or else chemical admixtures (e.g. superplasticizers) were added to the composites, or both [7–9,12,13,15,17,19–21]. Investigations into the recycling of secondary stainless steel slag by incorporating it as a SCM in cement composites have shown that the use of such slag can result in positive environmental effects [4].

However, the reaction mechanisms of secondary metallurgical slags as SCMs in cement composites are not yet well understood, which is true also for the hydration products formed over longer time intervals. This means that it can be relatively hard to predict the physico-mechanical properties of such composites, as well as any potential modifications which may be needed. For this reason it has been very difficult to forecast the long-term performance of cement composites which incorporate secondary metallurgical slags. Thus more detailed knowledge is needed in this field in order to boost the commercialization and beneficial use of slags of this type in the building and construction industry.

The aim of this work was to provide a detailed study of the compositional, structural, and activity characteristics of secondary metallurgical slag obtained from two different refining processes of stainless steel production, and of its influence as a SMC on the properties of cement composites, without the use of chemical admixtures. In order to verify the utilisation potential of the investigated slag as it is manufactured, directly after industrial recycling (at present the steel plant recycles the investigated slag for use in hydraulically bound applications in geotechnical engineering), the slag was not laboratory pre-treated in any way (e.g. by screening or grinding, separation, stabilization). On a laboratory scale slag can be treated relatively easily, but such treatment means that additional work has in reality to be performed in the field. Any additional subsequent treatment of individual construction products components by the producer leads to the higher energy consumption and subsequently higher costs. In order to boost recycling of this kind of slag in the construction and civil engineering sector, we investigated its possible usage as a cement supplement precisely in the form as it was received from the producer. In order to compare the effect of secondary stainless steel slag to that of conventional SCMs, the properties of cement composites made with the investigated slag were compared to those in which a limestone filler was used as a SCM. Blended cement composites were further compared to the reference cement composites (without supplements). The limestone filler was selected as SCM for comparison, due to its low reactivity, as it was expected that the reactivity of the investigated stainless steel slag would be low.

2. Materials and methods

2.1. Raw materials

Secondary metallurgical slag generated at the Acciaierie Bertoli Safau (ABS) steelworks, Italy was used for the investigations described in this paper [4]. It consisted of a mixture of slag derived from a vacuum oxygen decarburization process and ladle furnace slag, with an approximate weight ratio of 40:60. It was blended together in the molten state, which is the standard practice used at this steelworks. After deposition on the temporary outdoor stockpile, the slag was slowly air cooled, quenched (approx. 0.5 h), and aged (for approx. 3 months). It was then subjected to crushing, a metal removal process, and milling in order to achieve a gradation of 0/2 mm. Approximately 50 kg of the slag was sampled from the final roofed stockpile according to SIST EN 932-1 [22]. Portland cement CEM I 52.5R which satisfied the requirements of SIST EN 197-1 [23] was also used, as well as a limestone filler, which was obtained from the dust collection systems of the Mali Medvejk quarry, which is located in western Slovenia.

The particle size distribution of the raw materials was determined by a combination of dry sieving (particles > 400 μm) according to SIST EN 933-1 [24], and laser diffraction analysis (particles < 400 μm) in isopropanol, using a CILAS 920 laser (Cilas, Orléans, France). The density of these raw materials was determined using the pyknometer method (SIST EN 1097-7 [25] for both the slag and the limestone, and the method described in the standard SIST EN 196-6 [26] for the cement.

The Brunauer, Emmet, and Teller (BET) surface area of the slag and the limestone filler, was determined by nitrogen gas sorption using ASAP 2020 equipment (Micromeritics, Norcross, Georgia). The samples were evacuated at 105 °C with an evacuation rate of 0.67 kPa/s until a final vacuum of 2 Pa was achieved. The BET surface area was obtained by applying the Barret, Joyner, and Halenda (BJH) method, and the Halsey equation. Chemical analyses of the used raw materials were performed by means of inductively coupled plasma mass spectrometry (ICP-MS), after aqua regia digestion. The accuracy of the results thus obtained was verified by using certified reference materials, as well as blanks and repeated measurements.

The non-carbonate fraction (acid insoluble residue) of the limestone filler was determined according to ASTM D3042 [27].

The mineral phases in the raw materials were characterized by X-ray diffraction (XRD). All the XRD analyses were performed by using a PANalytical X'Pert PRO MPD diffractometer (PANalytical B.V., Almelo, the Netherlands), in Cu Kα1 configuration. Data were collected at room temperature over a 2θ range from 7° to 70°, using scanning steps of 0.033° 2θ. X'Pert HighScore Plus software (PANalytical B.V.), involving a PDF database as a source of reference data in order to identify the crystalline phases of the investigated samples. Quantitative phase analysis was performed by the Rietveld method, using Topas Academic V4.1 software (Burker-AXS) and the ICSD database.

The microstructural and selected mineralogical features of the slag and the limestone filler were investigated both on rough samples and on polished cross-sections, by scanning electron microscopy (SEM) using a JEOL 5500 LV (Tokyo, Japan) microscope, equipped with energy dispersive spectroscopy EDS (Oxford instruments, UK). The low-vacuum mode was used, the pressure in the chamber amounting to 12–13 Pa and the accelerating voltage to 20 kV.

In order to perform a detailed mineralogical composition of the slag, some other complementary test methods were used, such as Fourier Transform Infrared Spectroscopy (FTIR). The transmission infrared spectra of disked samples were recorded using a Perkin Elmer Spectrum 100 spectrometer across the range from 4.000–400 cm^{-1}, with a resolution of 4.0 cm^{-1} and 64 scans. Samples were mixed with pre-dried FT-IR grade KBr (Aldrich Chem. Co., St. Louis, MO, USA), at a ratio of approximately 1:200. Thermogravimetric (TG-DTG) analyses, too, were run on a Q5000IR instrument (TA Instruments, Inc., New Castle, DE, USA) at a rate of 10°/min from room temperature up to 1.000 °C, using an air flow of 25 mL/min. The results (given in%) were calculated by integrating the corresponding parts of the derivative thermogravimetric curves (DTG) and recalculating them to correspond to the ignited mass at 1000 °C. The TG and DTG curves were analysed by means of TA Instruments' Universal Analysis 2000 software package. The exact integration limits were determined by means of PeakFit software.

Since activity is an important characteristic of slag when used as a SCM in blended cement composites [28], it, too, was evaluated. As no standard exists for the determination of an activity index for this type of slag in the case of applications in cement-based materials, it was decided to apply the standard SIST EN 15167-1 [29] for ground granulated blast furnace slag (GGBFS).

In order to assess the self-cementing (hydraulic) capacity of the investigated slag, a slag paste (SP) was produced by mixing the slag with water at a ratio of 2:1 by weight [7]. SEM/EDS of the fracture surfaces of the slag paste after 28 days of hydration was carried out, as well as XRD analysis.

2.2. The cement composite specimens

Pastes and mortars in which 30% of cement by mass was replaced by slag were prepared. Additionally, in order to establish a basis for comparisons, pastes and mortars in which 30% of the cement by mass was replaced by a limestone filler were prepared, as well as reference 100% PC based pastes and mortars. The water/binder ratio in all the investigated pastes and mortars was selected to be 0.5. Data about the mixing proportions of the cement composites are shown in Table 1.