HYDRAULIC AND LEACHING BEHAVIOUR OF BELITE CEMENTS PRODUCED WITH ELECTRIC ARC FURNACE STEEL SLAG AS RAW MATERIAL


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Three belite-rich cements consisting of a clinker made with 0 (BC), 5 (BC5) and 10 wt. % (BC10) electric arc furnace steel slag (EAFS) as raw material, were studied for their hydraulic and leaching behaviour. Hydration behaviour was studied by FTIR, TG/DTG and SEM analyses. The cements with EAFS resulted in a higher C2S/C3S and C4AF/C3A ratio compared to the reference body. As a result, the rate of hydration was low at early days whereas the structure was porous with scattered AFm and C–S–H crystals. At 28 days, a comparable dense microstructure consisting largely of C–S–H is observed in all mortars. Leaching was studied for V and Cr by means of tank test according to standard NEN 7345. The results showed V release below 2 μg/l. Chromium release calculated per 24 h was 1.4 µg/l in BC5 and 2.4 µg/l in BC10, which is much lower than the parametric value of 50 µg/l specified by the European Directive for drinking water (98/83/EC).

INTRODUCTION

Cement production, due to energy requirements and due to the main reaction (decarbonation of limestone), results to a combined amount of approximately 0.9 kg CO2 per kg of clinker produced [1]. Apparently, a reduction in limestone content in the raw meal would lead to lower CO2 emissions. This resulted in scientific interest towards innovative types of cement [2], more specific, to belite type cements the last 20 years [3]. This type of cement, unlike the conventional OPC, consists of higher percentage of belite (C2S) and lower of alite (C3S). In addition to the above, alternative raw materials rich in CaO and low in CO2 content, such as metallurgical slags, can also contribute in meeting the goal of 50 % reduction in CO2 emissions by 2050 [4].

The use of metallurgical slags in cement is not new. Indeed, ground granulated blast furnace slag is one of the most widely used supplementary cementitious materials nowadays in blended Portland cements. However, a number of other ferrous and non-ferrous slag exist as well that find limited or no use in cement making. Depending on the slag, specific problems hinder this possibility. These problems relate either to production, microstructure and hydraulic properties of the clinker or to health and safety aspects of the final cement. A substantial amount of work is available already in the literature [5-7].

Steel slags, namely basic oxygen furnace slag, electric arc furnace slag and secondary metallurgical slag, set an interesting example. In Europe, of a production of approximately 22 Mt in 2010, only 6 % was used in cement production [8]. The main issue relates to the presence of heavy metals, Cr in particular. In the European Union (EU) a directive regarding Cr (VI) came into effect in 2003 and prohibits the use or supply of cements containing more than 2 ppm water-soluble chromium by mass of cement [9]. Indeed, a number of adverse health effects, ranging in severity, have been associated with Cr (VI) exposure. According to NIOSH [10] all Cr (VI) compounds are considered potential occupational carcinogens. In practice, reducing agents, such as ferrous sulphate, either the monohydrate (FeSO4·H2O) or heptahydrate (FeSO4·7H2O) form, or stannous sulphate (SnSO4) are added to control the oxidation state of chromium [11]. Still, it is of interest to note that the EU directive shall not apply to the placing on the market for, and use in, controlled closed and totally automated processes in which cement and cement-containing preparations are handled solely by machines and in which there is no possibility of contact with the skin [9]. Thus, precast concrete applications, using the typically late-strength belite cements, could be an option, provided that end-of-life environmental criteria are also met.

In this study, two were the main targets: the monitoring and the understanding of the hydration properties of the produced clinkers and the study of Cr and V leaching from the mortars.
EXPERIMENTAL

Limestone, flysch and EAFS were used as raw materials. Flysch is a sedimentary deposit consisting of thin beds of sandstone, shale and clay and is widely used as a raw material in the cement production. The chemical analysis of the raw materials is presented in Table 1. Three types of clinker were prepared, one reference, BC, and two with 5 wt. % and 10 wt. % EAFS addition named BC5 and BC10 respectively. The mineralogical phases of the clinkers were calculated using the Bogue equations and measured by Rietveld method (Table 2). In order to achieve high belite cement, lime saturation factor (LSF) was adjusted in the range of 78 % to 83 % [12]. The obtained raw meals were composed of limestone/flysch/EAFS (in wt. %): 84.0/16.0/0.0, 80.5/14.5/5.0 and 77.0/13.0/10.0 for BC, BC5 and BC10 respectively.

For the preparation of the raw meal for clinkers’ production, raw materials were individually milled at a particle size below 90 µm, blended together and homogenised and mixed with water until a workable paste was reached out of which pellets of 15 mm to 20 mm diameter approximately were formed by hand. Drying of the pellets was performed for 24 h at 110°C, followed by calcination at 1000°C for 4 h. The chosen clinkering temperature, was 1380°C with 40 min soaking time [13]; a Super Kanthal electric resistance furnace was used. Fast cooling was applied by means of simultaneous air blowing and crushing with a hammer.

The crystalline phases of the clinkers were identified by X-ray diffraction analysis (D5000 Siemens). Diffraction patterns were measured in 20 range of 10° to 70° using CuKa radiation of 40 kV and 30 mA, with a 0.01° step size and step time of 1 deg/min. Qualitative analysis was performed by the DIFFRACplus Eva® software (Bruker-AXS) based on the ICDD Powder Diffraction File. The mineralogical phases were quantified using a Rietveld-based quantification routine with the TOPAS® software (Bruker-AXS) [14]. Table 2. Discrepancies were observed between the results obtained by Bogue and those by Rietveld. The most significant was Bogue’s underestimation of C_s and overestimation of C_tS. These are attributed to the fact that Bogue’s method is based on ideal stoichiometries for the clinker phases, without taking into consideration solid solutions. On the other hand, Rietveld analysis can reflect the changing conditions induced by the different raw materials as well as the non-equilibrium conditions during firing and cooling. Nonetheless, the qualitative trend is soundly predicted by Bogue.

For the hydration studies, clinkers were ground to a particles’ fineness of about 4000 cm^2/g (400 m²/kg) to 4100 cm^2/g (410 m²/kg) (Blaine method [15]), and mixed with 5 wt. % gypsum (particle size < 90 µm). Preparation of the specimens was done according to EN 196-1 [16]. The weight ratios of cement/CEN standard sand used was 1:3 and that of cement per water was 2:1. Mixing was done for a specific time as required by the standard, followed by casting in standardised moulds of 40 mm × 40 mm × 160 mm in size. Curing was performed for 24 h at 20°C with a relative humidity (RH) above 90 %, and then the samples were demoulded and stored under water. Details for the physico-mechanical properties can be found elsewhere [13]. For the study of the reaction products, hydration was halted by immersing crushed pieces from the mortar beams after 2, 7 and 28 days, in an acetone bath for 2 h approximately, followed by drying at 70°C for 24 h [17]. The hydrated products were analysed by thermogravimetry (TGA Q50, TA Instruments, heating rate of 10°C/min up to 980°C in static air [17]) and FTIR (PerkinElmer Spectrum BX) using the KBr technique. For the latter, thin and transparent pellets were prepared by mixing 1 mg of powdered sample with 150 mg KBr and uniaxial pressing at 7 t. The parameters of the measurements are as follows: wave-number range from 600 cm⁻¹ to 4000 cm⁻¹, 4 scans, resolution 4.0 cm⁻¹ and interval 1.0 cm⁻¹. For the microstructural studies, SEM was employed (gold coated samples, JSM 6300, software (Bruker-AXS)).

Table 1. Chemical composition of raw materials, in wt. %.

<table>
<thead>
<tr>
<th>Oxides</th>
<th>EAFS</th>
<th>Limestone</th>
<th>Flysch</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>32.52</td>
<td>48.90</td>
<td>5.55</td>
</tr>
<tr>
<td>FeO_{total}</td>
<td>26.31</td>
<td>1.00</td>
<td>5.90</td>
</tr>
<tr>
<td>SiO_2</td>
<td>18.11</td>
<td>9.00</td>
<td>58.25</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>13.30</td>
<td>1.36</td>
<td>13.75</td>
</tr>
<tr>
<td>MnO</td>
<td>3.94</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>MgO</td>
<td>2.53</td>
<td>0.65</td>
<td>2.86</td>
</tr>
<tr>
<td>Cr_2O_3</td>
<td>1.38</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>P_2O_5</td>
<td>0.48</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>TiO_2</td>
<td>0.47</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>SO_3</td>
<td>0.44</td>
<td>n.d.</td>
<td>0.05</td>
</tr>
<tr>
<td>BaO</td>
<td>0.14</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Na_2O</td>
<td>0.13</td>
<td>0.10</td>
<td>1.10</td>
</tr>
<tr>
<td>K_2O</td>
<td>n.d.</td>
<td>0.15</td>
<td>2.50</td>
</tr>
<tr>
<td>V_2O_5</td>
<td>0.06</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>LOI</td>
<td>&lt; 0.50</td>
<td>38.00</td>
<td>9.80</td>
</tr>
<tr>
<td>Total</td>
<td>99.81</td>
<td>99.16</td>
<td>99.76</td>
</tr>
</tbody>
</table>

LOI: loss on ignition, n.d.: not determined

Table 2. Calculated (Bogue) and measured (Rietveld) mineralogical composition of the produced clinkers, in wt. %.

<table>
<thead>
<tr>
<th>Phases</th>
<th>BC</th>
<th>BC5</th>
<th>BC10</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_s</td>
<td>27.43</td>
<td>35.3</td>
<td>22.39</td>
</tr>
<tr>
<td>C_tS</td>
<td>54.96</td>
<td>47.4</td>
<td>56.16</td>
</tr>
<tr>
<td>C_A</td>
<td>9.13</td>
<td>8.7</td>
<td>7.54</td>
</tr>
<tr>
<td>C_AF</td>
<td>8.49</td>
<td>7.5</td>
<td>13.90</td>
</tr>
<tr>
<td>CaO_{free}</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.07</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Total 100 100 100 100 100.
Jeol). The identification of crystalline hydration products by XRD analysis was not practically possible due to high amount of quartz available in the matrix as the XRD patterns show high intensity peaks of crystalline quartz and very low intensity peaks of hydrated phases.

The leaching of the mortar blocks cured for 28 days was studied by means of the tank leaching test [18]. Mortar blocks (40 mm × 40 mm × 60 mm) were added in sealed containers, using distilled water (pH 7) as a leachant. The leachant \( V_{\text{water}}/V_{\text{sample}} = 5/1 \) was renewed at 8 different times, that is: 0.25; 1; 2.25; 4; 9; 16; 36 and 64 days. The results are expressed as mg/m\(^2\) (Figure 5).

The leachate at the scheduled period was immediately filtered through a 0.45 µm membrane filter (Porafil®) and analysed for Cr and V by atomic absorption spectroscopy (AAnalyst 200, Perkin Elmer) with a lower detection limit of 0.002 mg/l.

RESULTS AND DISCUSSION

FTIR of cement hydrated mortars

FTIR spectra of the cement mortars after different curing periods are presented in Figure 1. A slight difference in the region of 650 cm\(^{-1}\) to 800 cm\(^{-1}\) specific to Si–O vibration band, \( Q_1 \) bending [19] is visible between curing days and cement types. The Si–O stretching generated \( Q_2 \) units, between 970 cm\(^{-1}\) to 1200 cm\(^{-1}\) due to C–S–H [20] overlapped at early days with monosulfate and ettringite vibration due to the S–O stretching band. Broader peaks at 1440 cm\(^{-1}\) due to C–O \( v_3 \) asymmetric stretching band and at 1630 cm\(^{-1}\) specific to carbonate bending band with CH [21] and traces of water [22] are in all cement mortars. These carbonate phases are also observed in TG/DTG graphs at temperature range between 500°C to 980°C. Between 3400 cm\(^{-1}\) to 3450 cm\(^{-1}\) a weak intensity band for the BC10 at 2 days compared to BC and BC5 can be observed due to a decrease of Ca(OH)\(_2\) [22] content, coming most probably from alite mineral. The aforementioned range is becoming broader with the reaction time due to the contained molecular water [22, 23]. An intense narrow band between 3450 cm\(^{-1}\) to 3600 cm\(^{-1}\), attributed to the symmetric and asymmetric \( v_1 \) and \( v_3 \) stretching vibration of O–H group specific to CH [23] becomes broader with reaction time due to water [21]. No shift of the peaks is visible between the cements containing slag and the reference one.

TG/DTG analysis of cement hydrated mortars

The TG and DTG curves of BC, BC5 and BC10 cement mortars after 2, 7 and 28 days of hydration are given in Figure 2. The mass loss between 50°C and 200°C is associated with interlayer C–S–H gel water loss [24, 25] overlapping with AFm and Aft hydration phases (at early days). At early days (2 and 7) gypsum dehydrates at about 125°C and at the same time is consumed by the formation of AFm and Aft [26]. Gypsum dehydration can be identified by the small weight loss in the DTG graphs at \( \sim 125^\circ \text{C} \). The rate of hydration...
increases gradually with hydration period in the cement mortars which determine a higher mass loss starting from 7 days onwards, as confirmed also by FTIR analysis. This phenomenon is due to the participation of C₃S phase in the hydration process which develop high C–S–H hydration product. Between 400°C to 500°C, the mass loss is associated with the dehydroxylation of portlandite (CH) [17, 27] and is decreasing as both, slag content and hydration period increase. At 28 days the weight loss of CH further decreases due to carbonation.

Figure 2. TG and DTG profiles of cement mortars hydrated for different curing periods: a) BC, b) BC5 and c) BC10.
As the slag content increases more carbonation occurs as identified by the mass loss between 500°C to 980°C. This phenomenon is most probably caused by the reaction between CH extensively formed due to high C₂S content, and carbon dioxide prior examination. Some authors suggested that this range of temperature may be attributed also to the final stage of C–S–H dehydration [17, 24]. Others claim that the decarbonation of CH containing CaCO₃ comprises more peaks with possible different shapes that correspond to more or less thermally stable calcium carbonates and dissociate at a lower temperature (520°C to 780°C) than that of CaCO₃ coming from natural sources (e.g. limestone between 780 to 980°C) [28]. Due to the very low content of MgO, Table 2, it was not possible to ascertain any hydration products such as brucite or Mg-carbonates. The hydration reaction of all samples was found to occur slowly with time, specific to belite type cements. The weight loss of C–S–H dehydration is higher in BC type cement and slightly decreases as slag increases. No new hydration products were found in BC5 and BC10 type cements compared to BC. Considering that the C–S–H dehydration occurs at slightly different temperatures between samples cured up to 7 days (< 100°C) and samples cured for 28 days (~ 100°C), we assume that different types of C–S–H have been formed, as mentioned elsewhere [29], and/or there have been changes in the hydration state of the AFm phase (at early days) as mentioned by Taylor [17].

**SEM analysis of cement hydrated mortars**

Secondary electron images (SEI) of the hydrated mortars after different curing periods are presented in Figure 3. In Figure 4, SEI of hydrated BC10 at 2 and 28 days are seen, revealing the presence of AFt (Figure 4a) and calcite crystals (Figure 4b), originating most probably from carbonated CH. BC at 2 days presents subhedral C–S–H crystals formed from the reaction of C₃S with water, and flakes of AFm (monosulfate = C₃A•CaSO₄•12H₂O) coming from the reaction of C₃A with

![Figure 3. Secondary electron micrographs of BC cement mortar: a) 2 d, b) 7 d, c) 28 d, BC5: d) 2 d, e) 7 d, f) 28 d and BC10: g) 2 d, h) 7 d, i) 28 days of hydration.](image-url)
water and the added gypsum [11]. Ettringite crystals were only seen in few cases (Figure 4a). The most plausible hypothesis is that, in the presence of gypsum, in the first 5 - 6 hours, the AFt nucleation is favoured, \((\text{AFt, trisulfate} = \text{C}_3\text{A}^*3\text{CaSO}_4*3\text{1}-3\text{2H}_2\text{O}) [30]\), limiting the precipitation of AFm which tends to occur in the later stages of hydration, a day or two after mixing [11, 31]. At 7 days, in the case of BC, AFm flakes are no longer present due to the lower C3A content and C–S–H crystals are more compact due to the higher C3S content compared to the slag containing cements. BC5 and BC10 reveal a higher porosity mortar matrix at early days (2 and 7) of hydration, with scattered crystals of C–S–H and flakes of AFm, due to a slow hydration rate. As the slag content increases in the raw meal, the rate of hydration at early days is visibly decreased, most probably due to higher content of C4AF and lower of C3A and C3S in BC10 and BC5 compared to BC. In all cases, at 28 days, compact and dense crystals of C–S–H are observed due to the participation of C3S in hydration. Crystals of CH were also occasionally found. In BC10 cement mortar, calcite crystals were seen in the micrographs (Figure 4b) as identified also by TG/DTG analysis.

**Leaching: tank test**

The released concentration of Cr from mortar blocks (µg/l) compared with the parametric value of Directive 98/83/EC (µg/l) is expressed in Table 3, whereas in Figure 5, the cumulative concentration of chromium leached after different leaching time is presented. In the case of V, the released quantities were below the detection limit (2 µg/l) of the atomic absorption spectrometer used. Increasing the EAFS content in the raw meal, the normalised release of Cr per 24h increases from 1.4 µg/l in BC5 to 2.4 µg/l in BC10. Most probably, in both cases, part of the Cr was eventually immobilised either in the mineralogical phases formed during clinkering or in the hydrates of the cement matrix, as has been also claimed by other authors [32]. The released concentration of Cr per 24h in both, BC5 and BC10 was well below the parametric values (50 µg/l) given in the Directive for drinkable water [33]. In addition, the leaching trend of Cr release is comparable for both BC5 and BC10 (Figure 5). Considering the oxidation of Cr to Cr (VI) during the clinkering process and the influence on environment during leaching [34], it may be possible that a reducing agent will be required to secure that the leachable Cr in the mortars does not exceed the maximum limit of 2 ppm specified in the European Directive [9].

<table>
<thead>
<tr>
<th>Samples</th>
<th>LΣ64d/24h/mortar (µg l⁻¹)</th>
<th>Parametric value (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC5</td>
<td>1.4</td>
<td>50</td>
</tr>
<tr>
<td>BC10</td>
<td>2.4</td>
<td>50</td>
</tr>
</tbody>
</table>

**Figure 4.** Secondary electron micrographs of BC10 cement mortar: a) 2 d, b) 28 days of hydration.

**Figure 5.** Cumulative concentration of chromium leached from the hydrated BC5 and BC10 cement mortars, after different leaching time.
CONCLUSIONS

The major findings can be summarised as follows:

● The presence of EAFS in 5 and 10 wt. % was found to slow down the hydration process when compared to the reference sample.

● In the samples prepared with EAFS addition, the $C_3S/C_A$ ratio increases.

● At 28 days, a dense microstructure consisting largely of $C-S-H$ is observed. This morphology appears comparable in all three cements studied and is attributed to the participation of $C_3S$ phase in hydration.

● AFm hydration products are visible only at early days.

● No new hydration products were found in BC5 and BC10 mortars when compared to BC.

● As the slag content increases, Cr leaching is also increasing but an important part remains eventually immobilised in the structure. The quantity of V leached was below the detection limit of the atomic absorption spectrometer used ($< 2 \mu g/l$).

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REFERENCES