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Properties of hydraulic paste of basic oxygen furnace slag

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ABSTRACT

Basic Oxygen Furnace (BOF) slags are by-products of the conversion of pig iron to steel. They mainly contain C_2S, C_2F, $Fe_{1-x}O$, CaO, $Ca(OH)_2$ and $CaCO_3$. According to their chemical composition they are a valuable mineral resource as additions in certain hydraulic binders. This paper presents a hydration study of the BOF slag pastes preserved at different temperatures and in different environments. Pastes are characterized by X-ray diffraction and scanning electron microscopy. The compressive strengths of hydrated pastes are given at 7, 28, 90 and 190 days. Results show that – BOF slags containing 40% of C_2S – have attractive mechanical properties. Hydration tests under water showed a pastes swelling due to the hydration of CaO contained in BOF slags. A lime extinction procedure was proposed as alternative to standard PR NF EN 13282-2. This approach is more effective for these materials: the volume expansion of pastes cured in water is avoided and the compressive strengths are thus significantly improved.

1. Introduction

Basic Oxygen Furnace (BOF) slags are by-products of pig iron refining. The operating principle of the basic oxygen furnace is to blow oxygen in order to oxidize carbon and then reduce its content in pig iron. During this operation, lime is introduced to fix undesirable elements in slag and protect refractory lining. At the end of the conversion BOF slag is separated from steel by densimetric separation and poured in casting pit where it is slowly air cooled. Depending on the grade of steel produced, 100–200 kg of BOF slag are generated per ton of steel produced [1]. Thus, in France for example, 1.2 millions of tons were produced in 2005.

BOF slags have good mechanical properties [2]. They have been valued as aggregates in road engineering. Unfortunately this use is restricted because of their high free lime content which causes uncontrolled volume expansions [3]. Some studies concerning aggregates degradation, volumetric instability and BOF slag swelling are underway to optimize their use in granular mixtures [4–6]. Only few investigations on hydraulic activity of BOF Slag pure pastes are reported in the literature to our knowledge [1,7].

The mineralogical composition of BOF slag is as follows: 40–55% C_2S, 20–30% C_2F, 10–13% $Fe_{1-x}O$, 1–7% CaO, 1–8% $Ca(OH)_2$, 2–4% $CaCO_3$ [8]. The three last phase's contents depend on the sample age. Indeed, when materials are finely ground, calcium oxide reacts with moisture in the air to form hydrated lime $Ca(OH)_2$. This last mineral reacts with ambient CO_2 to form calcite ($CaCO_3$) [9]. These phenomena may change or decrease the reactivity of the materials.

The calcium silicate C_2S is present in BOF slag as the β polymorph which is the reactive form present in clinker. The C_2S hydration is similar to that of C_3S but it is much slower. The hydration products are mainly calcium silicate hydrate CSH and Portlandite $Ca(OH)_2$. CSH are the most abundant hydration products on which depend the mechanical properties of a cementitious paste. Portlandite forms large crystals whose presence reduces the compactness of the structure and limits the compressive strength of hardened material [10]. However it plays an important role in early age performance and compressive strength.

Impure calcium ferrite C_2F usually contains Alumina; the presence of C_4AF phase in BOF slag cannot be excluded [11]. This last phase is also present in clinker. Its main hydration products are: $C_2(A,F)H_8$, $C_4(A,F)H_{13}$ et $C_3(A,F)H_6$. This phase may have a different chemical composition in the BOF slags, due to the variation of Alumina and impurities contents in C_2F phase.

As a consequence of the latent hydraulic properties of β-C_2S and C_2F phases and the high iron oxide content, BOF slags have poor reactivity [12]. However the early age mechanical performances of BOF slags hydrated pastes may be improved by calcium chloride ($CaCl_2$) [13].

The present investigations relate to BOF slag pastes characterization and to the follow-up of their compressive strengths. The objective is to evaluate the behavior of hydrated BOF slags and consider the valorization of these materials in hydraulic binders. Two different curing environments were investigated: under water and in saturated wet atmosphere. Samples were kept at 20, 40, 60 and 80 °C and tested at 28, 90 and 180 days. These different temperatures were investigated in order to accelerate the hydration reaction and prevent pastes behaviors in longer term.

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2. Materials and methods

2.1. Material

Three BOF slags, from different origins, are investigated in this paper: BS1, BS2 and BS3. Their chemical compositions, as established in a previous paper [13], are given in Table 1.

Most attention is given to the BS1 and BS2 samples. They are chosen for their high C_2S content: 40.3% and 54.9% respectively. In addition, they differ in CaO and $Ca(OH)_2$ contents; these two values are nearly equivalent for BS1; BS2 is richer in CaO.

BS3 is studied for comparison. Its C_2S content is low. Conversely, its $Ca(OH)_2$, $CaCO_3$ and CaO contents are higher.

Representative sampling of different sizes were performed for tests. The materials were crushed, ground with equal grinding duration and sieved to 0–125 μm size.

2.2. Experimental procedures

Particle size distribution is obtained by the laser particle size technique. Results are present in Fig. 1.

Before the pure pastes confection, slaking lime procedure was applied on the BOF slag powders according to the PR NF EN 13282 standard. This procedure must be applied to materials containing free lime. It consists on free calcium oxide hydration by adding the estimated amount of water required per calculation (stoichiometric amount), without initiating any hydration process of other components. BOF slag powder and water are slowly mixed in a standard mixer during 5 min. The CaO hydration is achieved when the temperature of slaked sample reaches a maximum value. Complementary tests are required to validate the slaking procedure (see PR NF EN 13282).

The pastes were prepared by mixing BOF slag powders (0–125 μm) with water in a standardized mixer in accordance with the cycle of the NF EN 196 standard. The water/BOF slag ratio of paste was 0.25. With this ratio, the three BOF slag pastes have almost normal consistency according to the standard NF EN 196. Pastes were then poured into cylindrical molds Ø34 h34 mm and kept at 20, 40, 60 and 80 °C. They were then cured in water or in a 96% RH atmosphere until they reached the desired age.

The compressive strengths tests were performed at 7, 28, 90 and 180 days after polishing the bearing surfaces.

The pastes breaks were used for chemical characterization by X-ray diffraction. Their hydration was stopped with acetone. Specimens were then dried at 40 °C and were ground for the X-ray diffraction analyses.

The crystalline phases were identified using a X-ray Diffractometer (XRD) using a copper anticathode. The X-ray diagram obtained has been exploited by the diffraction software Plus – EVA®. The morphology of hydrated pastes was observed using Scanning Electron Microscopy (SEM).

Table 1
Chemical composition of BOF slag investigated [13].

% Weight	BS1	BS2	BS3
C_2S	40.3	54.9	25.9
C_2F	30.3	22.5	27.7
FeO	11.9	13.1	7.5
$CaCO_3$	2.1	2.4	6.5
SiO_2	5.5	0	13.8
$Ca(OH)_2$	4.8	2.6	13.4
CaO	5.0	8.3	5.1

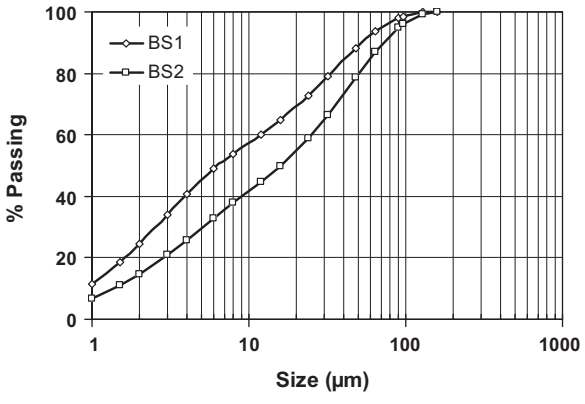

Fig. 1. BS1 and BS2 laser particle size distributions.

3. Results

3.1. Hydraulic behavior in saturated wet atmosphere

3.1.1. X-ray characterization

X-ray diffraction patterns of hydrated BS1 pastes at 20, 40, 60 and 80 °C are respectively presented on Figs. 2–5. They show the evolution of the mineralogical composition from the 1st to the 90th day of hydration.

At 20 °C, (Fig. 2), no significant consumption of the C_2S phase during the first 28 days is observed. The hydration is slow. The hydrated phase Epidote $Ca_2FeAl_2Si_3O_{12}(OH)$ (peak 6) appears from the 1st day and grows until the 28th day. At this maturity, a CSH type phase $Ca_2(SiO_3)(OH)_2$ (peak 7) is also identified as well as Portlandite (peak 2). At 90 days, the three formed hydrated phases are less visible thus showing recent developments. Calcite is well developed and the intensity of the diffraction peaks related to calcium silicate (C_2S – peak 3) has decreased.

At 40 °C, (Fig. 3), the samples behavior is similar to that described above, but the evolution is faster. The first days of hydration, a CSH phase containing Al and Fe appears "$Ca_3AlFe(SiO_4)(OH)_8$" (peak 6), in addition to Epidote. Simultaneously, a consumption of C_2S (peak 3) and the development of Portlandite (peak 2) are observed. At 28 days, C_2S phase is almost completely consumed and Epidote disappeared. At 90 days, the calcium silicate disappears. Portlandite is partially carbonated, and therefore, calcite is developed.

At 60 °C, (Fig. 4), C_2S (peak 3) phase is partially consumed from the first day. In parallel, $Ca_3AlFe(SiO_4)(OH)_8$ (peak 7), Portlandite $Ca(OH)_2$ (peak 2) and $CaCO_3$ (peak 1) appear, showing then a rapid reactivity of BOF slag at this temperature. By 7 days the calcium

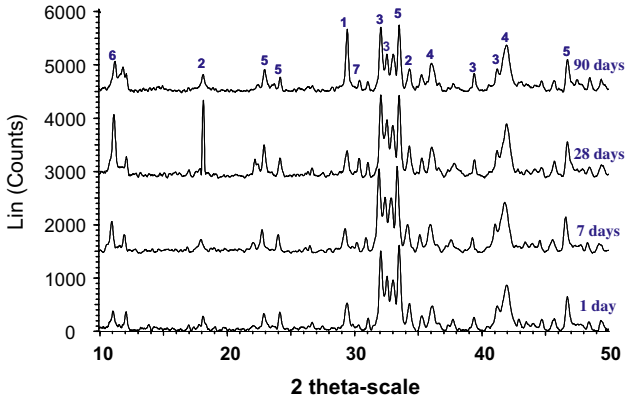

Fig. 2. X-ray diffraction patterns of BS1. Saturated wet atmosphere. 20 °C 1 – $CaCO_3$, 2 – $Ca(OH)_2$, 3 – C_2S, 4 – FeO, 5 – C_2F, 6 – Epidote,7 – $Ca_2(SiO_3)(OH)_2$.