



# 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.

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## 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  $\beta$  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  $\beta$ - $C_2S$  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  $\mu m$  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  $\mu m$ ) 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).

## 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.

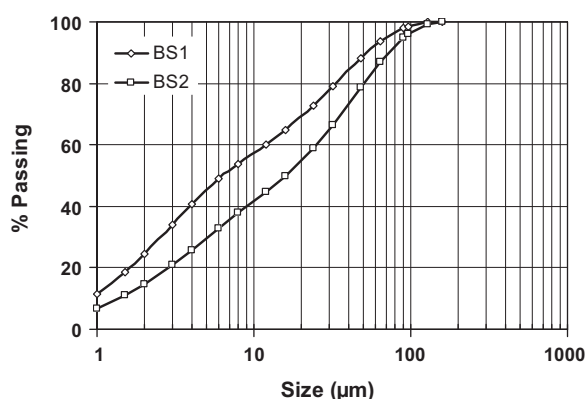
At 20 °C, (Fig. 2), no significant consumption of the  $C_2S$  phase during the first 28 days is observed. The hydration is slow. The hydrated phase Epidote  $Ca_2FeAl_2Si_3O_{12}(OH)$  (peak 6) appears from the 1st day and grows until the 28th day. At this maturity, a CSH type phase  $Ca_2(SiO_3)(OH)_2$  (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.

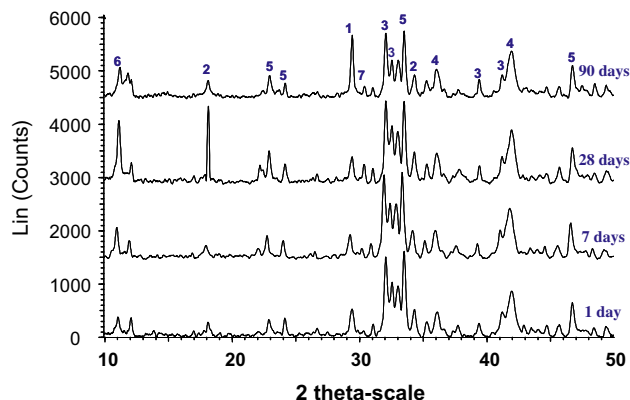
At 60 °C, (Fig. 4),  $C_2S$  (peak 3) phase is partially consumed from the first day. In parallel,  $Ca_3AlFe(SiO_4)(OH)_8$  (peak 7), Portlandite  $Ca(OH)_2$  (peak 2) and  $CaCO_3$  (peak 1) appear, showing then a rapid reactivity of BOF slag at this temperature. By 7 days the calcium

**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.



**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 –  $Ca_2(SiO_3)(OH)_2$ .

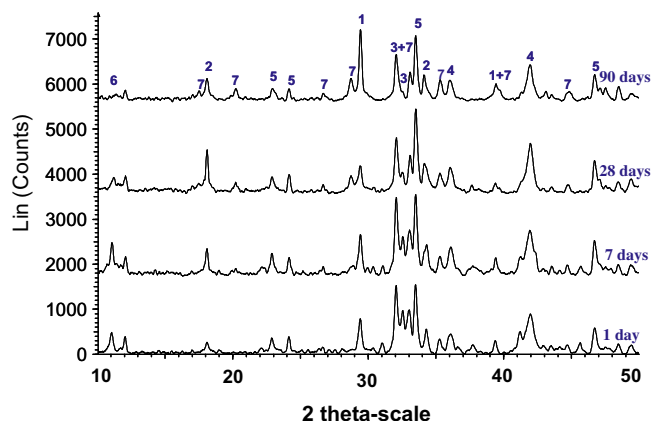


Fig. 3. X-Ray Diffraction Patterns of BS1. Saturated wet atmosphere. 40 °C 1 –  $\text{CaCO}_3$ , 2 –  $\text{Ca(OH)}_2$ , 3 –  $\text{C}_2\text{S}$ , 4 –  $\text{FeO}$ , 5 –  $\text{C}_2\text{F}$ , 6 – Epidote, 7 –  $\text{Ca}_3\text{AlFe(SiO}_4\text{)(OH)}_8$ .

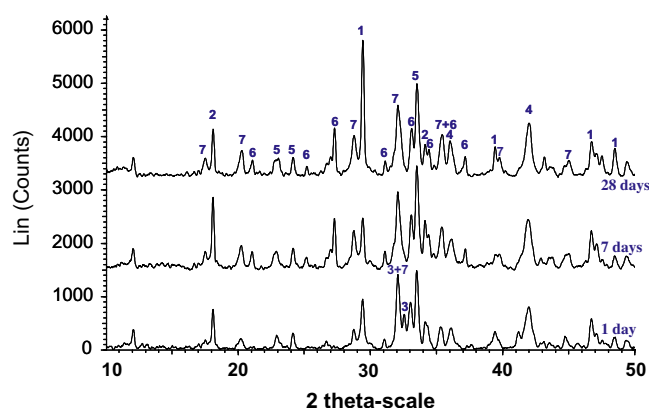


Fig. 4. X-ray diffraction patterns of BS1. Saturated wet atmosphere. 60 °C 1 –  $\text{CaCO}_3$ , 2 –  $\text{Ca(OH)}_2$ , 3 –  $\text{C}_2\text{S}$ , 4 –  $\text{FeO}$ , 5 –  $\text{C}_2\text{F}$ , 6 – CSH, 7 –  $\text{Ca}_3\text{AlFe(SiO}_4\text{)(OH)}_8$ .

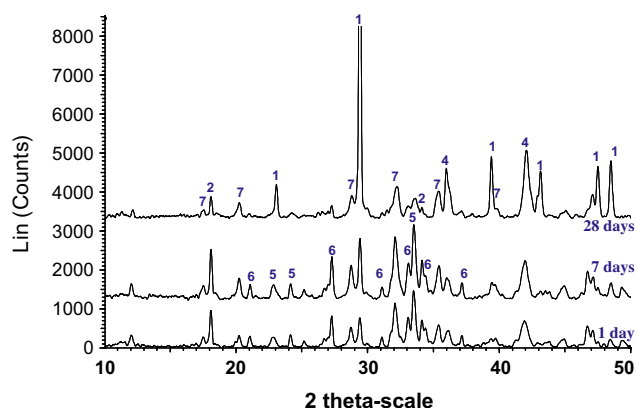


Fig. 5. X-ray diffraction patterns of BS1. Saturated wet atmosphere. 80 °C 1 –  $\text{CaCO}_3$ , 2 –  $\text{Ca(OH)}_2$ , 3 –  $\text{C}_2\text{S}$ , 4 –  $\text{FeO}$ , 5 –  $\text{C}_2\text{F}$ , 6 – CSH, 7 –  $\text{Ca}_3\text{AlFe(SiO}_4\text{)(OH)}_8$ .

silicates have totally reacted. The hydration products are  $\text{Ca}_3\text{AlFe(SiO}_4\text{)(OH)}_8$ ,  $\text{Ca(OH)}_2$  and  $\text{Ca}_2\text{SiO}_4\text{H}_2\text{O}/2\text{CaOSiO}_2\text{H}_2\text{O}$  (peak 6). At 28 days, the carbonation of Portlandite is observed.

At 80 °C, (Fig. 5), the hydration is very fast. From the first day, the calcium silicate totally reacts producing  $\text{Ca}_3\text{AlFe(SiO}_4\text{)(OH)}_8$  (peak 7),  $\text{Ca}_2\text{SiO}_4\text{H}_2\text{O}/2\text{CaOSiO}_2\text{H}_2\text{O}$  (peak 6) and  $\text{Ca(OH)}_2$  (peak 2). At 7 days, the hydrated phases formed on the first day continue to grow and calcite appears in quantity (peak 1). At 28 days, the diffraction peaks related to hydrated products disappear for the

benefit of those well-developed of calcite. This shows a very important carbonation process at this temperature. The  $\text{C}_2\text{F}$  phase disappears and only the peaks of  $\text{CaCO}_3$  and  $\text{Fe}_{1-x}\text{O}$  (peak 4) are obvious.

The BS2 X-ray patterns are not given in this paper. The same hydration products are observed. Only CSH phases identified at 60 °C and 80 °C do not appear.

### 3.1.2. Microstructure of hydration products

The hydrated products of BOF slag pastes were observed by scanning electron microscopy, after 90 days of hydration at different temperatures. Analyses were performed on a wide range observation at different scales. Some photographs are shown in Fig. 6 (20 °C). The main phases observed are a CSH gel (Fig. 6a), Portlandite  $\text{Ca(OH)}_2$  (Fig. 6b) and Calcite  $\text{CaCO}_3$  (Fig. 6c). The Epidote is less present (Fig. 6d) and it was detected by comparison of SEM morphology presented by Kalinoswski [14].

### 3.1.3. Compressive strength of BOF slag pastes

Mechanical properties of hydrated BS1 and BS2 pastes are respectively given in Fig. 7a and b. They show the development of compressive strength at 7, 28, 90 and 180 days and for samples cured at 20, 40, 60 and 80 °C. The average values are given with the standard deviation.

At 20 °C, the compressive strengths increase over time. They reach a plateau of 27 MPa after 90 days of hydration for the sample BS2 (Fig. 7b), while those of the sample BS1 (Fig. 7a) continue to rise (37 MPa at 90 days and 50 MPa at 180 days). This gradual evolution is in agreement with the XRD analysis of hydrated phases, described above, which showed that the hydration at 20 °C is slower and progressive. At this temperature, the hydraulic phases, especially  $\text{C}_2\text{S}$ , are not totally consumed, even at 90 days. This results in mechanical strengths growth beyond 90 days.

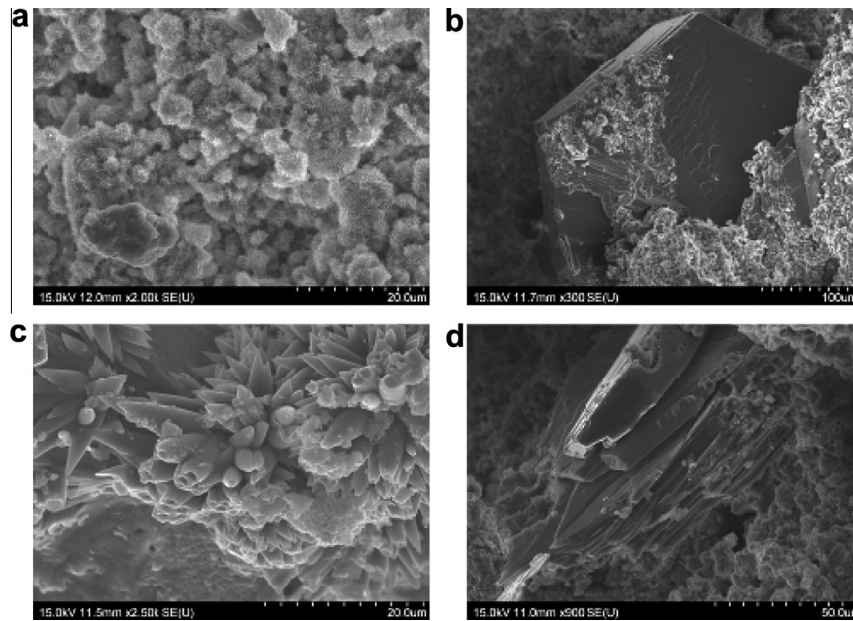
At 40 °C, the hydration is faster compared to 20 °C as confirmed by XRD analysis previously presented. As at 20 °C, BS1 paste performances continue to rise until 180 days. At this maturity, they reach 40 MPa. Those of BS2 paste reach a maximum of 25 MPa at 90 days then fall significantly (18 MPa at 180 days). These observations show that temperature only accelerates the young age mechanical resistance. After 90 days their values are lower to those obtained at 20 °C.

At 60 °C, the mechanical strength of BS2 paste at 90 days have unfortunately not been measured. At this temperature, most samples were carbonated involving an expansion and a weakening of the material structure. For BS1 sample (and BS2 probably) the maximum is reached at 28 days. The X-ray diffraction analysis has shown a fast reactivity: a total consumption of  $\text{C}_2\text{S}$  at 7 days followed by a carbonation clearly visible from 28 days. In general, the values are low compared to those measured at 20 and 40 °C: the maximum strength at 28 days was 21 and 13 MPa for BS1 and BS2 respectively.

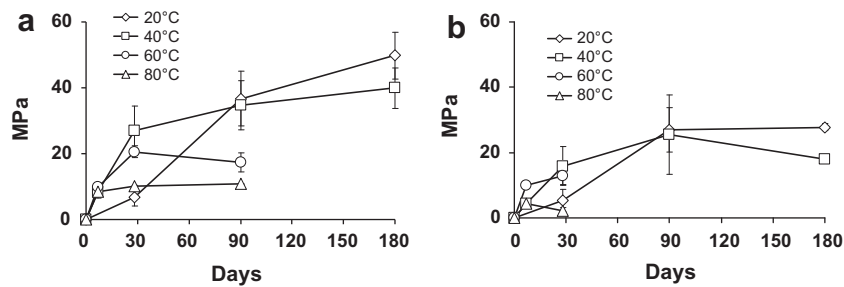
At 80 °C, the abundant calcite formation as of the first days of hydration has involved the swelling of specimens and, consequently, their physical destruction. Mechanical strength at 90 days could not be measured for the BS2 sample. The strengths obtained are very low compared to those measured previously.

The carbonation effect on the mechanical performances of some construction materials was investigated by several authors [15,16]. They show that:

- For adobe bricks with a lime content higher than 10%, calcite is formed abundantly and consumes CSH: it results in a mechanical strength fall [15].
- For Portland cement, hydrates compositions change for a temperature higher than 50 °C. As a consequence, the volume of solid decreases and the porosity, which is the first factor influencing the mechanical performance, increases. This results in a dramatic decrease in the mechanical strength [16].



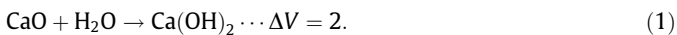
**Fig. 6.** BS1 hydrates morphology after 90 days hydration at 20 °C (saturated wet atmosphere). (a) CSH, (b) Portlandite, (c) alcite and (d) Epidote.



**Fig. 7.** Compressive strengths of hydrated BOF slag pastes (a) BS1 and (b) BS2.

### 3.2. Hydraulic behavior under water

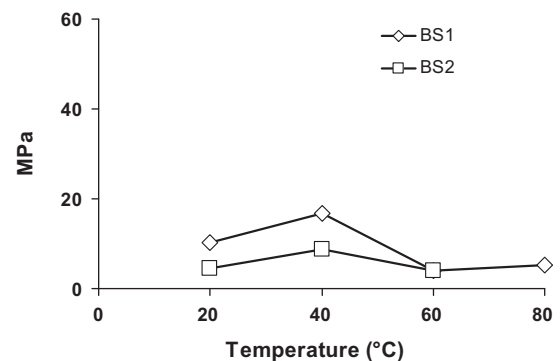
For all temperatures, a significant swelling of pastes was observed as early as the first day of hydration. It resulted in the emergence of a paste on the top of the specimen, like a “muffin”. The upper part of the sample was analyzed by X-ray diffraction: calcium hydroxide  $\text{Ca}(\text{OH})_2$  has been mainly identified. This phase is, probably, the  $\text{CaO}$  hydration product since this reaction is immediate and accompanied by a volume expansion ( $\Delta V$ ).



Thus it demonstrates that the slaking lime procedure, according to standard PR NF EN 13282-2, is partial.

To determine the specimen's compressive strength, the paste on the top of the sample was removed and bearing surfaces have been regularized. Results are given in Fig. 8. They show that mechanical performances in water are lower to those obtained for samples cured in saturated wet atmosphere.

As for conservation in saturated atmosphere, the values at 28 days reach a maximum at 40 °C: 17 MPa and 9 MPa for BS1 and BS2 respectively. It should be remembered that samples stored in a humid atmosphere under the same conditions reach respectively 35 and 25 MPa for BS1 and BS2 (Fig. 7). This difference is clearly due to physical alterations caused by pastes swelling due to  $\text{CaO}$  hydration.



**Fig. 8.** Compressive strength of BS1 and BS2 BOF slag cured in water at different temperatures during 28 days.

## 4. Discussions

### 4.1. Hydraulic products of BOF slag

The investigation on BOF slag pure pastes showed that the main mineral phases have a slow hydraulic reactivity. Only the  $\text{C}_2\text{S}$  consumption was observed simultaneously to the development of CSH and  $\text{Ca}(\text{OH})_2$ . The  $\text{C}_2\text{F}$  phase partially reacts at ambient temperature; its whole consumption is observed at 80 °C after 28 days of



hydration. Four hydrated products were mainly identified. Their formation depends on the hydration temperature and the conservation time.

#### 4.1.1. Epidote $\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}(\text{OH})$

It is an unstable phase in the BOF slag pastes. Indeed, it is not observed at temperatures above 40 °C. At 20 °C it appears and develops up to 28 days. It disappears completely at 90 days. At 40 °C, it disappears before 28 days. Its development is very fast and it is not correlated with the consumption of the  $\text{C}_2\text{S}$  phase (Figs. 2 and 3). It seems thus that the calcium silicate does not interfere in its formation. Considering the Epidote composition, its formation is probably related to the  $\text{C}_2\text{F}$  hydration, which contains aluminum as impurity and quartz.

To verify the Epidote formation origin, a hydration test on salicylic acid extracted BOF slag was performed. The salicylic acid extraction dissolves the  $\text{C}_2\text{S}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaO}$  phases. Extracted powder only contains the  $\text{C}_2\text{F}$ ,  $\text{Fe}_{1-x}\text{O}$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$  phases. A normal consistency paste has been made with this powder and kept at 40 °C in saturated wet atmosphere. X-ray patterns are given on Fig. 9.

On the first hydration day at 40 °C, Epidote formation is observed (peak 7). This proves that this hydrated product results from the  $\text{C}_2\text{F}$  (peak 5) hydration and its interaction with  $\text{SiO}_2$  (peak 8) present in BOF slags. The Epidote is thus less present in BS2 sample whose  $\text{SiO}_2$  content is lower (§ 3.1.1).

A second hydrated product of the  $\text{C}_2\text{F}$  phase is  $\text{Ca}_3\text{Fe}_2\text{Si}_{1.15}\text{O}_{4.6}(\text{OH})_{7.4}$  (peak 6). This is the same kind as the  $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$  phase previously observed on the steel slag hydrated with diffraction peaks slightly shifted (peak 7, Fig. 3).

#### 4.1.2. CSH with Fe and Al: $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$

This phase is formed at 40 °C and above this temperature. It appears from the 7th day at 40 °C and earlier for higher temperatures (1 day at 80 °C). Its formation is always accompanied by a consumption of the  $\text{C}_2\text{S}$  phase and by the crystallization of Portlandite. It is a CSH type phase containing Al and Fe. Other test on BOF slag hydration had also shown the production of a CSH phase contains Al and Fe [7]. The  $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$  is also developed for the sample BS2 hydrated under the same conditions.

#### 4.1.3. CSH: $\text{Ca}_2(\text{SiO}_3)(\text{OH})_2$ and $\text{Ca}_2\text{SiO}_4\text{H}_2\text{O}/2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$

The Hillebrandite  $\text{Ca}_2(\text{SiO}_3)(\text{OH})_2$  appears at 28 days of curing at 20 °C and disappears for longer maturities. CSH  $\text{Ca}_2\text{SiO}_4\text{H}_2\text{O}/2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$  is observed at 60 and 80 °C, but disappears after 28 days at 80 °C.

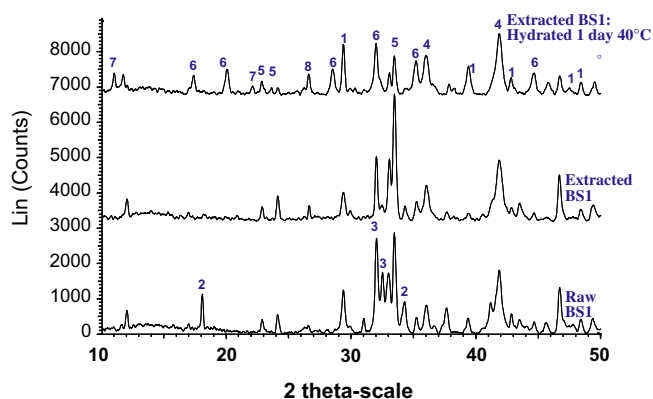


Fig. 9. X-ray patterns of raw BS1, extracted BS1 and 1 day hydrated BS1 at 40 °C 1 –  $\text{CaCO}_3$ , 2 –  $\text{Ca}(\text{OH})_2$ , 3 –  $\text{C}_2\text{S}$ , 4 –  $\text{FeO}$ , 5 –  $\text{C}_2\text{F}$ , 6 –  $\text{Ca}_3\text{Fe}_2\text{Si}_{1.15}\text{O}_{4.6}(\text{OH})_{7.4}$ , 7 – Epidote, 8 –  $\text{SiO}_2$ .

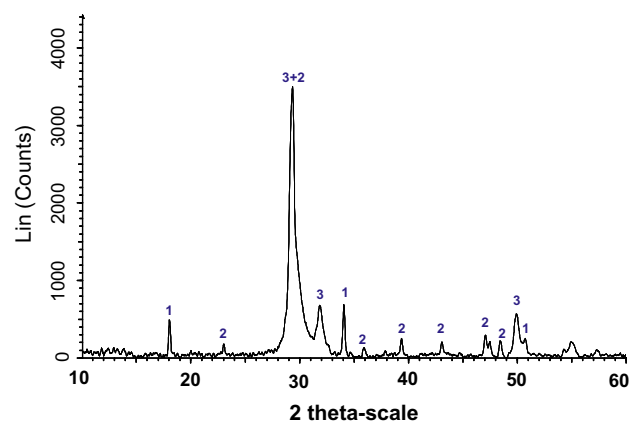


Fig. 10. Product of  $\text{CaO}$  and  $\text{SiO}_2$  hydration at 40 °C during 7 days 1 –  $\text{Ca}(\text{OH})_2$ , 2 –  $\text{CaCO}_3$ , 3 –  $\text{Ca}_{1.5}\text{SiO}_{3.5}\text{H}_2\text{O}/1.5\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ .

These two phases are only observed for the BS1 sample. As BS2 contains less  $\text{SiO}_2$ , we deduce that they may be produced by interaction between the  $\text{CaO}$  hydration and quartz. To confirm this hypothesis, a paste of  $\text{CaO}$  (commercial quicklime 99%) and  $\text{SiO}_2$  (silicon dioxide) was prepared. After 7 days conservation at 40 °C, a CSH type phase and Portlandite are observed (Fig. 10).  $\text{Ca}(\text{OH})_2$  is partially carbonated.

Those results confirm that CSH identified in BOF slag pastes may be produced by the reaction between free lime and quartz.

## 4.2. Effect of the chemical composition and of the powder fineness

Previous investigations on BOF slag's mechanical strength showed that BS1 sample is more resistant than BS2. Contradictorily BS2 has a higher  $\text{CaO}$  and  $\text{C}_2\text{S}$  content. Logic suggests that the opposite result is obtained, showing an increasing relationship between the mechanical strength and the  $\text{C}_2\text{S}$  content. To better understand the difference in the hydraulic behavior of these two materials, a third sample has been investigated under the same conditions. This BOF slag BS3 has a lower  $\text{C}_2\text{S}$  content and a higher  $\text{SiO}_2$  one (Table 1). 28 and 90 days compressive strengths are compared respectively in Fig. 11a and b.

BS3 has very low compressive strengths compared to those of the others BOF slags. The maximum values are reached at 90 days of hydration. They are equal to 5 and 6 MPa at 20 and 40 °C, respectively. These values show a very low hydraulic activity, probably because of its low  $\text{C}_2\text{S}$  content compared with those of BS1 and BS2.

These observations confirm that the hydraulic activity of BOF slag and mechanical properties they can reach are mainly due to  $\text{C}_2\text{S}$  phase (polymorph  $\beta$ ), whose hydration can be activated by temperature. The Epidote, produced by  $\text{C}_2\text{F}$  and silica hydration, does not contribute to the mechanical performance.

However, it is still surprising that BS1 compressive strengths are larger than those of the BS2 specimens, while the latter contains a greater amount of  $\text{C}_2\text{S}$  and lime.

All pastes are made with 0–125  $\mu\text{m}$  particle size powder. The specific surface area of BS1 and BS2 were then measured by the Blaine test. They are equal to 3800 and 3600  $\text{cm}^2/\text{g}$  for BS1 and BS2 respectively, indicating that BS2 is harder to grind. This may due to the  $\text{C}_2\text{S}$  phase presence, which has a high Vickers hardness [17].

The laser particle size distributions of both samples, shown in Fig. 11, confirm that BS1 includes a more abundant fine fraction. This difference of size grading explains thus the higher compressive strength values of the BS1 sample.

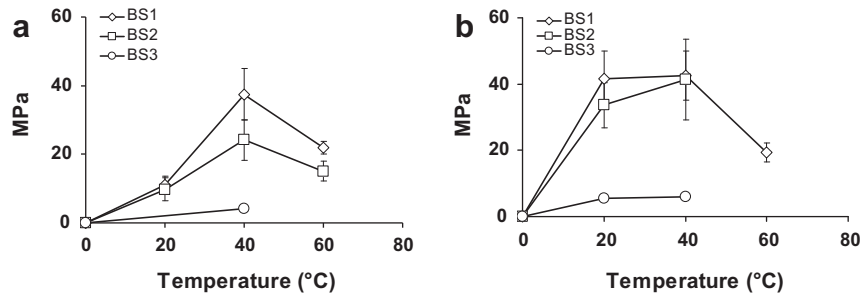


Fig. 11. BOF slag compressive strength at 20, 40 and 60 °C (a) 28 days and (b) 90 days.

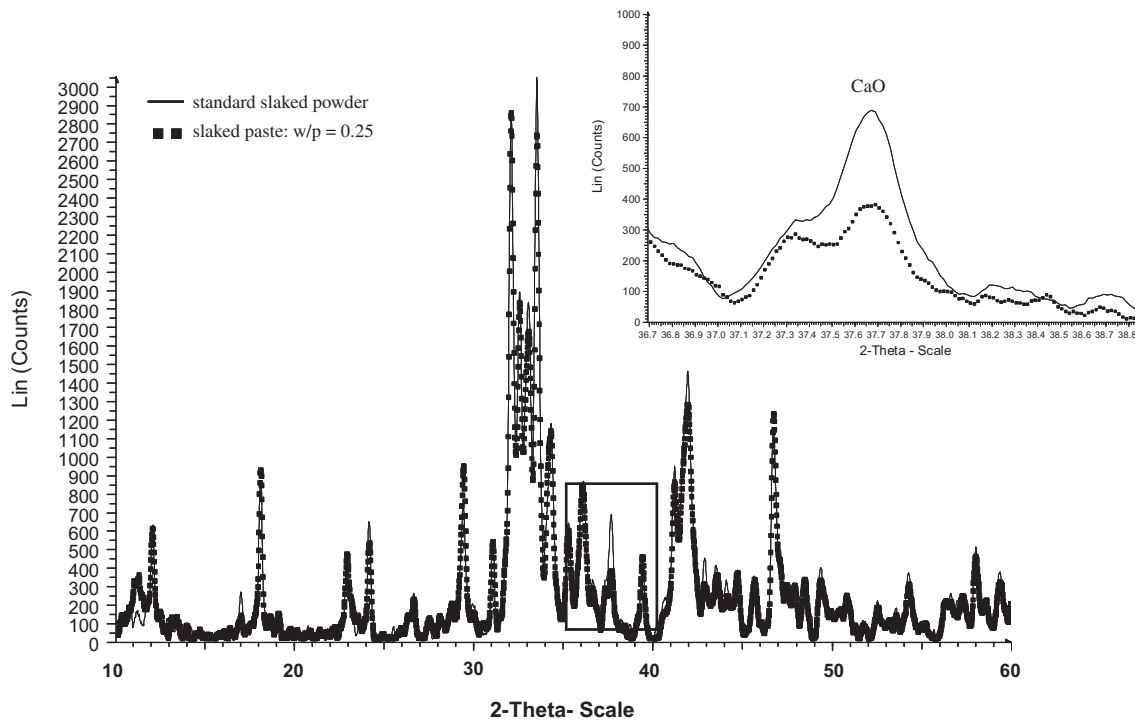


Fig. 12. X-ray diffraction patterns of slaked BOF slag powder and BOF slag slaked paste.

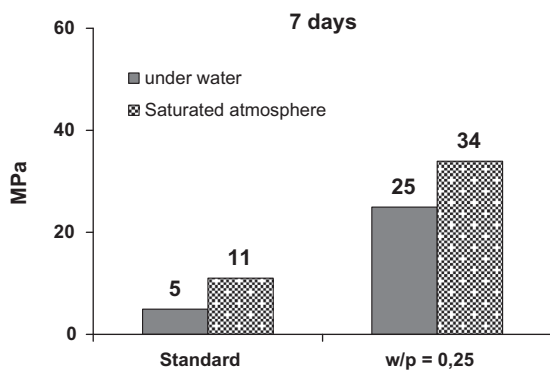


Fig. 13. Effect of standard and improved lime slaking procedures on the compressive strength of BOF slag pastes.

#### 4.3. The effect of the slaking lime procedure

The different analyses (XRD, compressive strength) performed on slaking powders showed that the standard lime slaking

procedure (PR NF EN 13282-2) is not suitable for BOF slag materials. Indeed, lime is trapped within the material and not easily accessible. Some tests were performed in order to improve the slaking operation and to obtain a homogenous powder.

The first test was to replace the automatic mixing by a manual slaking procedure. The principle is similar to the standard one, but the water was added gradually, by using a vaporizer during mixing. This was done manually to better homogenize the powder. Furthermore, other tests were performed in which the amount of extinctive water required by the standard was multiplied by 2, 3 and 4. For each extinction ratio, pure pastes were prepared and kept in water at ambient laboratory temperature (20 °C). A significant swelling was observed for all samples, including those slaked with 4 times a quantity of extinctive water.

The second test was the paste slaking using the standard mixer. The principle is to introduce at once the entire quantity of water expected to have the normal consistency, i.e.  $w/p = 0.25$ . The powder and water are slowly mixed during 5 min (standard procedure). The paste was then covered with a damp cloth to prevent water evaporation. After 30 min (the time needed for calcium oxide hydration, according to the PR NF EN 13282-2), paste was

mixed according to the standard cycle of cement pastes (EN 196-1). Pastes still had the normal consistency. Then they were poured into the cylindrical molds and kept in water and in saturated wet atmosphere for comparison.

X-ray diffraction patterns of the standard slaked powder and the slaked paste are given in Fig. 12. A magnification of the  $2\theta$  angle range corresponding to the CaO diffraction is shown inset. This figure shows that the CaO slaking is more effective when the procedure is applied on paste.

The lime slaking effect is clearly observed on pastes compressive strengths as shown in Fig. 13. This figure compares compressive strength of pastes slaked with the standard procedure and with  $w/p = 0.25$  ( $p$  corresponds to BOF slag powder), at 7 days. Strengths are multiplied by three for saturated wet atmosphere cured samples and by five for those cured in water. At 20 °C and for 28 days of hydration in water and in a wet saturated atmosphere, BOF slag pure pastes reached respectively 25 MPa and 34 MPa.

## 5. Conclusion

The hydration of BOF slag pure pastes in a wet saturated atmosphere was carried out on three samples of different origin at 20, 40, 60 and 80 °C. The results showed that it is the  $C_2S$  phase which hydrates mainly. Its hydration products confer attractive mechanical properties (50 Mpa) for samples with at least 40% of  $C_2S$ . BOF slag hydration is accelerated by temperature, but beyond 60 °C carbonation of hydrates is observed. A volume expansion of the pastes then appears as well as a fall of the compressive strengths. Grinding of the slags improves the compressive strengths significantly, particularly at young ages.

Hydration products are calcium silicate hydrates containing iron and aluminum. The most stable hydrate, which confers the mechanical resistance to hydrated pastes, is the  $Ca_3AlFe(SiO_4)(OH)_8$  phase. It is well developed after 28 days of hydration at 40 °C and the compressive strength corresponding to this maturity is equal to 30 MPa.

Other less stable hydration products have been identified as the Epidote  $Ca_2FeAl_2Si_3O_{12}(OH)$  ( $C_2F$  phase hydration product), CSH ( $Ca_2(SiO_3)(OH)_2$  and  $Ca_2SiO_4H_2O/2CaOSiO_2H_2O$ ). This CSH is only observed with samples with high  $SiO_2$  content and is produced by CaO and  $SiO_2$  hydration.

Hydration tests under water showed a pastes swelling due to the hydration of CaO contained in BOF slags. The lime extinction

procedure, applied according to standard PR NF EN 13282-2, is not effective for these materials. Further investigation found that the only way to hydrate CaO is to apply the slaking procedure on the slag paste, by using all water required to have a paste of normal consistency as extinctive water. The volume expansion of pastes cured in water is avoided and the compressive strengths are thus significantly improved.

## References

- [1] Mahieux PY, Aubert JE, Escadeillas G. Utilization of weathered basic oxygen furnace slag in the production of hydraulic road binders. *Constr Build Mater* 2008;28:742–7.
- [2] Motz H, Geisler J. Products of steel slags an opportunity to save natural resources. *Waste Manage* 2001;21:285–93.
- [3] Shi C, Qian J. High performance cementing materials from industrial slags – a review. *Resour Conver Recycl* 2000;29:195–207.
- [4] Lecomte A, Dao LP, Diliberto C. Valorisation des LAC dans les mélanges granulaires Partie. 1: un modèle de dégradation. *EJCE* 2011;15(6):889–913.
- [5] Lecomte A, Dao LP, Diliberto C. Valorisation des LAC dans les mélanges granulaires. Partie 2 : modélisation de la courbe d'expansion à la vapeur. *EJCE* 2011;15(6):915–38.
- [6] Lecomte A, Dao LP, Diliberto C. Valorisation des LAC dans les mélanges granulaires. Partie 3 : modélisation de l'expansion d'un mélange quelconque. *EJCE* 2012;16(6):635–49.
- [7] Wang Q, Yan P. Hydration properties of basic oxygen furnace steel slag. *Constr Build Mater* 2010;24:1134–40.
- [8] Belhadj E, Diliberto C, Lecomte A. Chemical, physical and mineralogical characterization of Basic Oxygen Furnace slag – BOF slag. *Euro Mediterranean Symposium On Advances in Geomaterial and Structure – Djerba*; 2010.
- [9] Belhadj E, Diliberto C, Lecomte A. Caractérisation des laitiers d'aciérie de conversion et suivi de leur évolutivité dans le temps. 28èmes Rencontres Universitaires de Génie Civil – La Bourboule du 2 au 4 Juin ;2010.
- [10] Altun A. Effect of  $CaF_2$  and  $MgO$  on sintering of cement clinker. *Cem Concr Res* 1999;29:1847–50.
- [11] Belhadj E. Valorisation des laitiers d'aciérie de conversion dans les liants hydrauliques routiers. Thèse UHP-Nancy; 2010.
- [12] Murphy JN, Meadowcroft TR, Barr PV. Enhancement of the cementitious properties of steelmaking slag. *Can Metall Quart* 1997;36(5):315–31.
- [13] Belhadj E, Diliberto C, Lecomte A. Characterization and activation of basic oxygen furnace slag. *Cem Concr Compos* 2012;31:34–40.
- [14] Kalinowski BE, Faith-El C, Schweda P. Dissolution kinetics and alteration of epidote in acidic solutions at 25 °C. *Chem Geol* 1998;151:181–97.
- [15] Millogo Y, Hajjaji M, Ouedraogo R. Microstructure and physical properties of lime-clayey adobe bricks. *Constr Build Mater* 2008;22:2386–92.
- [16] Lothenbach B, Matschei T, Möschner G, Glasser FP. Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. *Cem Concr Res* 2008;38:1–18.
- [17] De Souza VCG, Koppe JC, Costa JFCL, Marin Vargas AL, Blando E, Hübner R. The influence of mineralogical, chemical and physical properties on grindability of commercial clinkers with high  $MgO$  level. *Cem Concr Res* 2008;38:1119–25.