BASIC OXYGEN FURNACE SLAG (BOF SLAG): CHARACTERIZATION AND EVOLUTIVITY

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1. INTRODUCTION

BOF slag is a by-product of the conversion of pig iron to steel in a basic oxygen furnace (BOF). Depending on the raw material, 100-200Kg are generated per ton of steel [MAH, 08]. In 2005, 170 million tons were produced in the world (1.2 million tons in France). The principle of converting cast iron into steel is to blow oxygen to decrease carbon content. Lime is added in the converter in order to fix undesirable elements contained in pig iron and to protect the fire brick. At the end of conversion BOF slag is separated from steel by gravimetric separation.

BOF slag are still undervalued. A small amount is used by agriculture in amendment to neutralize soil acidity. Road engineering used to consume an important quantity as aggregate since these materials have good mechanical properties and a low cost [MOT, 01]. Unfortunately this use is restricted because of free lime content of BOF slag which causes uncontrolled volume expansions [CAI, 00]. Several studies concerning aggregates degradation, volumetric instability and BOF slag swelling, are underway to optimize their use [LEC, 11 1-2-3].

With a chemical composition similar to Portland cement one, the exploitation of BOF slag in some hydraulic binders can also be considered. They nevertheless have poor hydraulic properties, mainly because of their high content of iron oxide and the weak content of tricalcium silicate [MUR, 97]. Indeed, the wüstite ($Fe_{1-x}O$), which is one of the major phases of BOF slag does not react with water. Furthermore, when materials are finely ground, calcium oxide they contain reacts with air moisture to form hydrated lime $Ca(OH)_2$. This last mineral reacts itself with the ambient CO_2 to form calcite $CaCO_3$. Thus the CaO content decreases over time. These phenomena may change or decrease the reactivity of the unstable materials.

BOF slag valorisation requires previously a through physical and chemical characterization to have a good awareness of their properties. Most of the literature on this subject only relates to the qualitative characterization of BOF slag and the quantification of free lime content, due to the problem of expansion.

Investigations presented in this study are more complete because they relate to the identification and quantification of all mineral phases present in BOF slag (C_2S, C_2F, etc.). They were performed on a variety of products with different origins and ages (fresh and weathered productions).

2. EXPERIMENTS

2.1. Materials

The BOF slag studied are coming from different industrial plants and melts. After cooling and treatment they are reclaimed as 0/100 mm granulates with a minimum fine fraction.

BS1samples are a mixture of several melts from the same origin but with different ages:

– BS1F: Fresh production

– BS1W: Weathered production

BS2 samples are fresh products, from a second industrial plant and separated melts which differ by the free lime content. This parameter depends on the grade of steel produced:

– BS2H: High lime content

– BS2L: Low lime content

Representative sampling of large granulates were performed for analysis. They were crushed, ground and sieved to 0-125 m size.

2.2. Characterization procedures

The specific surface area was determined by the Blaine test according to the EN standard 196-6. The absolute density was measured by a hydrostatic weighing in a non-reactive liquid.

The X Ray Fluorescence technique is an emission of secondary X Rays characteristic of the atomic elements in the sample. It was used to determine the chemical composition of powders, expressed as a percentage of oxides.

The crystalline phases were identified using a X-pert pro X-ray Diffractometer equipped with a monochromator using a copper anticathode. The diffractogram obtained has been exploited by the diffraction software Plus - EVA®.

The crystallinity of samples was verified by a transmission electron microscope coupled to a microdiffraction and a chemical microanalysis.

The plan view of different phases in the grain slag was given by an electron probe microanalyzer and EDS analyses were performed to identify the minerals' chemical composition and impurities that may present.

The free lime content is found by acid-base titration. This method must be complemented by TGA-DTA (Thermo-Gravimetric Analysis coupled with Differential Thermal Analysis), in order to find out the hydroxide and oxide calcium content separately. This last method allowed us also to determine the carbonate ($CaCO_3$) content. Indeed, this technique allows to follow up and to quantify mass changes due to dehydration and decarbonation of samples as a function of temperature.

The main characteristic of steel slag is the high iron oxide content, which exists in both the di- and trivalent states. This content is found by redox titrations; FeII is titrated by a potassium dichromate solution $K_2Cr_2O_7$ in the presence of sodium diphenylamine sulphonate indicator.

$$6Fe^{2} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3}+ + 7H_2O \quad [1]$$

The FeIII is reduced to FeII by stannous chloride $SnCl_2$ in order to titrate both di and trivalent states contents.

The calcium silicate content is found by selective extraction. Calcium phases are dissolved by salicylic acid and the C_2S is calculated by difference with the already known lime content.

3. RESULTS AND DISCUSSIONS

3.1. Physical properties

The absolute density measured on these BOF slag equals 3700 kg/m^3 on average. This value is relatively high, due to the high iron content. Note here that, due the presence of iron oxide, a longer grinding time is needed comparing to the clinker one. The density is measured on a freshly ground powder; samples aging causes hydration and carbonation of free lime and, consequently, a decrease of density. This parameter may reach an average of 3300 kg/m^3 after 6 months aging.

The specific surface area of 0-0.125 mm fresh powder equals to almost 3800 cm^2/g.

3.2. Mineralogical characterization

The BOF Slag oxide composition, obtained by X Ray Fluorescence and compared to the clinker one, is shown in table 1.

These materials contain more than 80% of CaO, SiO_2 and Fe_2O_3. Despite the iron content, BOF Slag composition is close to the clinker one. The higher content of Fe_2O_3 is a major disadvantage for both physical and hydraulic properties since iron phases are inert with water contact. The chemical compositions of the four BOF slags studied are similar despite their diverse origins. The main difference is the Loss Of Ignition (LOI) value which is the mass loss at 1000°C. A high LOI value indicates the presence of hydrated and/or carbonated phases.

Figures 1 and 2 show respectively XRD patterns of BS1 and BS2 samples. The minerals phases are mainly, C_2S, C_2F, $Ca(OH)_2$, CaO, $Fe_{(1-x)}O$. Minor phases as $CaCO_3$, MgO and SiO_2 are identified in some cases.

X-ray diffraction (XRD) indicates that the major mineral in BOF slag is -C_2S. Unlike others slags, BOF slags contain in most cases the form [SHI, 02]. Usually, -C_2S changes to -silicate below 675°C, but this disintegration is not found in the presence of high "FeO" content.

The main difference between the two BS1 samples appears in calcic phases (figure 1):

– The calcite content is higher for BS1W slag due to the hydroxide calcium carbonation during weathering. This result is in agreement with the high LOI (Loss Of Ignition) value obtained by XRF (table.1)

– The hydroxide calcium content is higher for the BS1W. It is produced by the hydration of calcium oxide and calcium silicate.

The X-ray pattern of BS2 confirms that BS2H contains more lime phases (figure 2). The amount of calcite is relatively low since these slags are considered fresh ones.

Wt %	LOI	MgO	Al2O3	SiO2	P2O5	CaO	MnO	Fe2O3
BS1F	1.1	4.5	1.9	10.8	1.4	45.0	2.6	32.0
BS1W	8.3	5.5	1.9	8.6	1.4	40.1	2.0	30.8
BS2L	0.0	6.0	1.7	13.1	2.4	41.7	4.1	29.3
BS2H	0.0	7.5	2.1	11.3	2.0	42.9	3.7	28.3
K	0.2	4.3	4.7	20.8	0.2	63.6	0.1	3

Table 1 Chemical composition of BOF slag by XRF technique

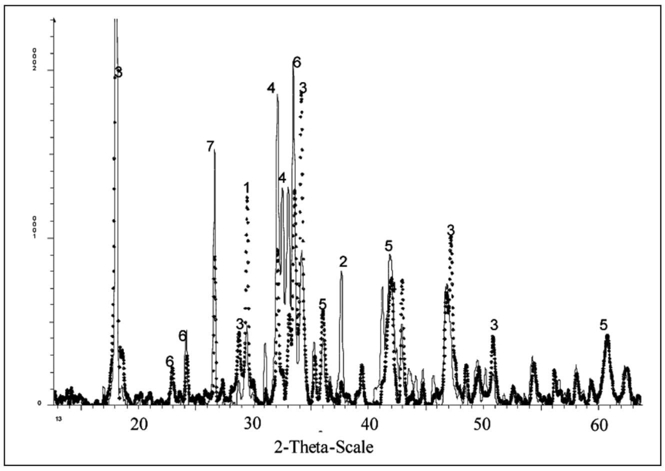

Figure 1: X-ray diffraction pattern of BS1; solid line BS1F, dotted line BS1W
1-CaCO$_3$, 2-CaO, 3-Ca(OH)$_2$, 4-C$_2$S, 5-FeO, 6-C$_2$F, 7-SiO$_2$

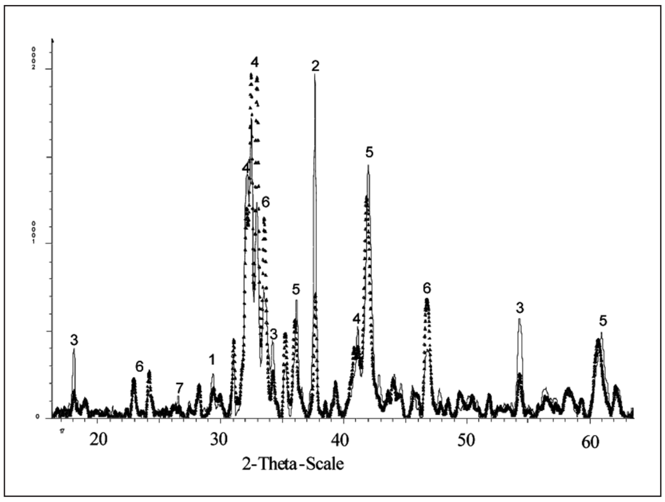

Figure 2 X-ray diffraction pattern of BS2; solid line BS2H, dotted line BS2L
1-CaCO$_3$, 2-CaO, 3-Ca(OH)$_2$, 4-C$_2$S, 5-FeO, 6-C$_2$F, 7-SiO$_2$

Most authors mention the presence of C_3S and C_4AF [MUR 97, MAH 08]. These two phases are hardly distinguishable in the XRD pattern because of peaks overlapping. However C_3S phase can stand out from C_2S by a peak at 1.76 Å which is not visible in the X ray pattern probably due to the low content of this phase. C_3S is especially present in BOF slag with a Ca/Si basic ratio higher than 2.7 [CAI, 00].

We note that no amorphous phase was detected by this technique. The transmission electron microscopy analysis showed that all samples are mainly crystallized. Only the C_2S phase containing phosphorus has a diffuse diffraction pattern which shows a low crystallinity.

The cooling rate may influence slag composition or the mineral phases present and, consequently, alter the mechanical properties of these materials [SRI, 06]. An amorphous phase can be formed with a 10°C/min cooling rate for the CaO-SiO_2-Al_2O_3 system, while its formation requires a more rapid cooling for the CaO-SiO_2-FeO one [DUR, 08]. BOF slag samples were then kept at 1250°C during 24h in an inert atmosphere and then cooled at 5°C/min. This cooling rate will allow a slow and complete crystallization of the samples phases, including that of a possible amorphous phase. Results highlighted the presence of a new crystalline phase with a chemical formula $Ca_5(PO_4)_2(SiO_4)_6$. No other crystalline phase appeared. The absence of any amorphous halo on the X-ray patterns shows that this phase, even if it exists, would be present only at a very low content which can not reasonably influence the hydraulic behavior of these materials.

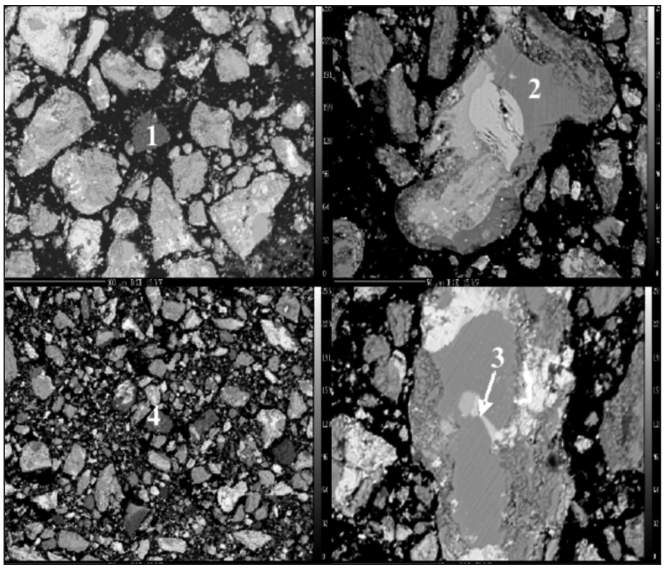

Figure 3 Plan view of BOF slag by microprobe analysis
1 : MgO – 2 : C$_2$S – 3 : C$_2$F – 4 : Ca(OH)$_2$

To evaluate the specific chemical compositions of phases identified above, the samples were characterized by the micro probe technique. A plan view, given in figure 3, shows the structural heterogeneity of BOF slag.

Generally, phases are intermixed in a grain. It is rare to observe independent phase as the grains of MgO and $Ca(OH)_2$ (grains 1 and 4 respectively in figure 3). Calcium silicates seem to be homogeneous phases with the Ca/Si ratio varying from 1.8 to 3.5 (grain 2). The average of Ca/Si ratio is 2.4; this means that the major phase is C_2S. The presence of C_3S is possible because of the relatively high Ca/Si ratio in some grains, but the content of this phase is too low to be detected with XRD. The average composition of silicate phases is given in table 2.

Wt % C_2S	Si	P	Ca	O	Ca/Si
	9-14	0.5-2	27-32	55-57	1.8-3.5

Table 2: Average atomic composition of C_2S phases

The only impurity detected in this phases is phosphorus. Geiseler shows that the C_2S can be present in solid solution with C_3P [GEI, 96].

Calcium ferrite (grain 3) is also a homogeneous phase with more or less high content in aluminum. The ratio of Fe/Ca is, in some points, close to the C_4AF phase one. This phase can be present in BOF slag [MAH, 08], but can not be identified in X ray diffraction due to the overlapping peaks with C_2F ones. The average composition of ferrite phases is given in table 3.

Wt % C_2F (Al)	Al	Ca	Ti	Fe	O	Fe/Al
	4-5	23-24	1-2.4	13-16	52-53	2.5-3.7

Table 3: Average atomic composition of C_2F phases

Most grains present solid solutions (Fe, Mg, Mn and Ca)O with variable contents, a common mineral in BOF slag [TSA, 07]. Tossavainen has identified by XRD two types of wustite solid solutions (Fe, Mn, Mg)O and a solid solution dominated by CaO [TOS, 07].

3.3. Chemical characterization

The residual lime content (CaO + $Ca(OH)_2$) expressed in equivalent CaO was measured by a glucose extraction and filtrate's titration by hydrochloric acid. This chemical titration includes also the free MgO content but this last one is neglected in our study since XRF results show a weak value and the micro probe technique confirm that it is mostly present in solid solution. This chemical titration is completed by a TGA technique in order to differentiate CaO and $Ca(OH)_2$. Two reactions can be distinguished in the temperature interval 20-800°C.

◊ 450°C: $Ca(OH)_2$ dehydration $Ca(HO)_2 \rightarrow CaO + H_2O$ [2]
◊ 750-800°C: $CaCO_3$ decarbonation $CaCO_3 \rightarrow CaO + CO_2$ [3]

According to the reactions (2) and (3) the content of $Ca(OH)_2$ and $CaCO_3$ can be calculated with mass balance. The results are given in table 4.

Wt %	Free lime	$Ca(OH)_2$	CaO	$CaCO_3$
BS1F	6,8	6,3	2,0	2,9
BS1W	7,8	7,3	2,3	4,0
BS2L	5,5	1,1	4,6	1,9
BS2H	10,3	2,9	8,1	2,6

Table 4: Calcareous phases content

From chemical titrations of FeII and FeIII and based on the fact that FeII is only present in $Fe_{(1-x)}O$ and FeIII in C_2F, these two phases contents are calculated and given in Table 5.

	"FeO" (%)	C_2F (%)
BS1F	11,9	30,3
BS1W	12,9	24,5
BS2L	11,5	20,2
BS2H	13,1	22,5

Table 5: Iron phases content

The last phase to quantify is calcium silicate. The method adopted is extraction of calcic phases with salicylic acid. Powder extracted was analyzed with XRD. C_2S, $Ca(OH)_2$ and CaO were dissolved by the acid and C_2F, $Fe_{1-x}O$, $CaCO_3$ and SiO_2 remain in the powder. C_2S and SiO_2 contents can be calculated with balance mass. The results are given in table 6. Metal iron is not considered in this calculation. It may be associated to SiO_2 content. This may explain the variability of this parameter.

3.4. Phases assessment

The compositions of studied samples are given in table 4. It should be noted that the chemical compositions of BOF slag are close despite their different origins and ages. It should be noted that some phases were neglected in this calculation such free MgO and iron metal whose contents are weak comparing to others minerals.

	C_2S	C_2F	FeO	$Ca(OH)_2$	CaO	$CaCO_3$	SiO_2
BS1F	41.8	30.3	11.9	6.3	2.0	2.9	4.7
BS1W	38.1	24.5	12.9	7.3	2.3	4.0	10.9
BS2L	52.0	20.2	11.5	1.1	4.7	1.9	8.5
BS2H	51.1	22.5	13.1	2.9	8.1	2.7	0

Table 6: Minerals contents in BOF slag

3.5. BOF slag evolutivity

The characterization of various BOF slag samples has shown that these materials have quite similar compositions, irrespective of their origins. But their chemical composition can evolve by hydration and/or carbonation of free lime and calcium silicate. Calcium oxide contained in the finely ground BOF slag reacts with moisture in the air to give hydrated lime Ca $(OH)_2$ which, itself, reacts with the ambient CO_2 to form calcite $CaCO_3$. Thus the CaO content decreases over time, this may alter the physical properties of these materials.

To investigate samples evolutivity, the $Ca(OH)_2$ and $CaCO_3$ contents were identified over time by thermogravimetric analysis. BOF slag powder, with 0/125 m particle size, was kept in an oven at 40°C and in air at ambient laboratory temperature. The results are shown in figure 4.

At 20°C, calcite $CaCO_3$ develops due to calcium hydroxide $Ca(OH)_2$ carbonation. However, the amount of $Ca(OH)_2$ phase remains almost constant. Its carbonation is simultaneously done with its formation by CaO hydration.

At 40°C the contents of the various phases do not evolve. An increase in carbonate content is rather expected since temperature accelerates the carbonation process. This must be due to a low humidity in the oven; this parameter affects the kinetics of carbonation. Indeed, a study has shown that the carbonation of the lime is 9-20 times faster in the presence of water vapor [NIK, 07]. This phenomenon requires a process of dissolution of $Ca(OH)_2$, and CO_2 is then more easily adsorbed on the grain surface by the OH^- ions.

4 CONCLUSIONS

The different complementary techniques used in this study were an original approach to quantify and qualify BOF slag's mineral phases. Four samples of two different origins were investigated. They have a similar chemical composition. The most significant difference between the two origins is the C_2S content, which is present in at least 38%. Dicalcium silicate was detected in the form of β-C_2S which is the active polymorph present in hydraulic binder. C_3S was also identified in same grains by micro-probe analysis but its content is so weak to be detected by XRD. The second mineral, mainly present, is C_2F. It always contains Al and can cover up C_4AF in XRD analysis.

Due to the presence of those minerals, BOF slags can be considered as suitable material in field of construction. However wustite, which is present in at least 11%, has no hydraulic properties. It also has the ability to take up to 27% calcium oxide. This last phase is trapped into solid solution and can not react.

Composition of BOF slag evolves once reduced to a fine powder. The carbonation of free lime is preferred in humid atmosphere where two reactions occur simultaneously:

– calcium oxide hydration $CaO + H_2O \rightarrow Ca(OH)_2$

– calcium hydroxide carbonation $Ca(OH)_2 + CO_2 \rightarrow CaCO_3$

This results in a significant decrease in the density of these materials and, probably, their mechanical properties.

The interpretation and comparison of results obtained for different slag revealed interesting points for their eventual reactivity. The complete methodology proposed in this work is an essential preliminary step to find the best way of their valorization in construction.

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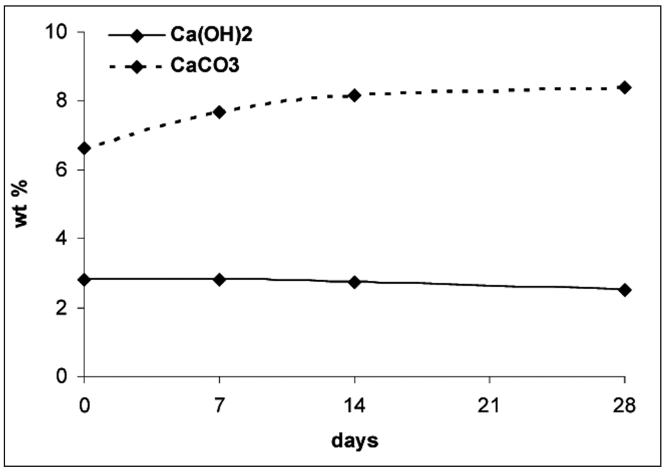

Figure 4a: BOF slag evolutivity at 20°C

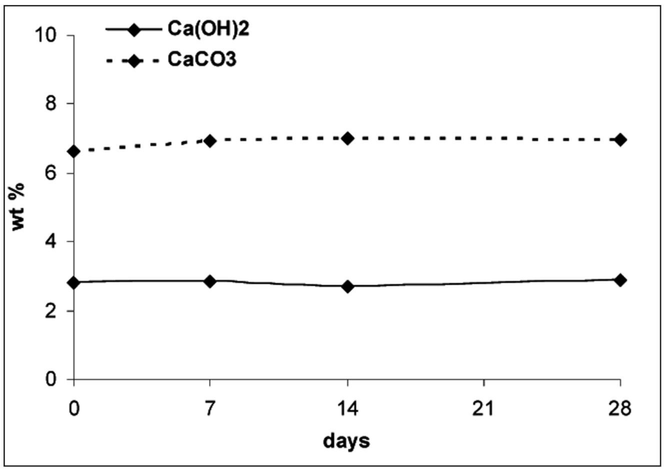

Figure 4b: BOF slag evolutivity at 40°C

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