Characterization of basic oxygen furnace slag and granite waste mixtures to Portland cement production

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Abstract

The aim of this paper is to analyze mixtures of basic oxygen furnace slag and granite waste in order to produce Portland cement. X-ray patterns were carried out in both the basic oxygen furnace slag and granite waste. Then, mixtures were prepared to obtain the binary basicity of 0.5, 0.9 and 1.2. The mixtures were melted at 1500°C. Two cooling steps were performed. The first cooling step was accomplished inside the furnace in order to determine the phases formed during the melting step. The second cooling process was carried out in water in order to obtain an amorphous structure. Images via scanning electrons microscopy and EDS spectrum were obtained for the mixtures cooling in water. The results showed that basic oxygen furnace slag contains a higher percent of CaO. A binary basicity of 4.6 was determined. The granite waste appeared as mainly a quartz phase. During the slow cooling step, silicates (akermanite and gehlenite) were formed. On the fast cooling step, amorphous structures were obtained. In addition, images obtained via scanning electrons microscopy showed glass structures. EDS spectrum indicated that the glass structures were composed for calcium silicates. Thus, the results suggest that mixtures using basic oxygen furnace slag and granite waste presented characteristics desirable for Portland cement production.

Keywords: Basic oxygen furnace, granite waste, solid waste, Portland cement.

1. Introduction

Increasing industrial production increases waste generation, which has a cost for its disposal such as transport to send it to the landfills and environmental control. Thus, the reuse of waste is an alternative for the companies.

In the metallurgical sector, solid, liquid and gaseous wastes are generated, such as sludge, dust and slag (from blast furnace and basic oxygen furnace) (Vieira *et al*., 2006). In this sector, several researches have been performed in order to reuse blast furnace slag (BFS) to produce Portland cement (Garcia *et al*., 2014; Heikal *et al*., 2015; Saade *et al*., 2015). The production of Portland cement approaches 3700-4000 Mt/y. This material is composed for SiO_2, Al_2O_3,

Fe_2O_3, CaO, MgO, SO_3, K_2O, Ti_2O_5, P_2O_5 (Sanjuán *et al.,* 2015; Ma *et al.*, 2015). According to Iacobescu *et al.*, (2015), the main phases detected in Portland cement are tricalcium silicate-3CaO.SiO_2 (C_3S), dicalcium silicate-2CaO.SiO_2 (C_2S), tricalcium aluminate-3CaO.Al_2O_3 (C_3A) and iron tetracalcium aluminate 4CaO.Al_2O_3.Fe_2O_3 - (C_4AF).

The use of basic oxygen furnace slag (BOFS) can be also an alternative to produce Portland cement, once contain CaO and SiO_2 (Goodarzi and Salimi, 2015). However, its use is restricted due CaO/SiO_2 relationship (around 4) and free CaO, which cause expansion and long time to stabilize the Portland cement (Arribas *et al.,* 2015). Besides, the free CaO decrease the slag vitrification, which can interfere on the hydraulic properties. BOFS shows little hydraulic activity due slow hydration from C_2S. Thus, addition range of 6-15% of Al_2O_3 in BOFS favor the C_2F and C4AF formation, which gives higher hydraulicity to Portland cement. In addition, research has showed that slag hydraulic activity increased to higher Al_2O_3/Fe_2O_3 relationship (CONJEAUD *et al.*, 1981). According to Lea (1970), increasing the CaO/SiO_2 favors the slag hydraulicity. However, increasing the CaO content increase also the viscosity. Such fact difficult the granulation and formation of a glassy structure.

In this way, granite waste (GW) may become a potential input on the Portland cement production, once contain higher SiO_2 and lesser CaO contents, as can be noted in Table 1. Such fact indicates a possibility to produce Portland cement, since decrease the BOFS basicity (CaO/SiO_2).

Thus, the aim of this paper is to characterize mixtures containing basic oxygen furnace slag and granite waste in order to produce Portland cement.

Elements (%)	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2
Junca *et al.*, 2015	65.9	13.4	1.4	1.0	4.2	2.6	4.4	-
Singh *et al.*, 2016	72.57	15.63	-	0.83	-	4.21	6.76	-
Tchadjié *et al.*, 2016	60.51	17.49	8.71	3.27	1.64	1.95	3.72	1.42
Hojamberdiev *et al.*, 2011	65.1	14.0	4.34	0.45	0.46	0.48	0.74	-

Table 1
Chemical composition of granite waste.

2. Materials and methods

Basic oxygen furnace slag and granite waste compositions have been published previously (Arrivabene *et al.*, 2012). Table 2 summarize the results. It is noted that BOFS is composed mainly for CaO (46.0%) and SiO_2 (10%), with binary basicity of 4.6. The granite waste contain mainly SiO_2 (59.6%) and Al_2O_3 (18.1%). Other elements were also determined in lesser percentages, such as MgO, MnO, Fe_2O_3, FeO, P_2O_5, Na_2O, K_2O and TiO_2. Thus, mixed between BOFS and granite waste can become an alternate to decrease the binary basicity in order to produce Portland cement.

Elements (%)	CaO	SiO_2	Al_2O_3	MgO	MnO	Fe_2O_3	FeO	P_2O_5	Na_2O	K_2O	TiO_2
BOFS	46.0	10.0	1.5	7.0	6.0	-	27.0	2.0	-	-	-
GW	4.6	59.6	18.1	2.8	1.0	4.8	-	-	3.1	3.7	0.9

Table 2
Chemical composition of basic oxygen furnace slag and granite waste.

To fulfil the characterization, X-ray patterns were obtained in order to determine the phases present in both materials. Tests were carried out using a Bruker diffractometer, equipped with Cu Kα (λ= 1,5418Å) tube. Scan range of 5-80°, step width of 0.2° and duration time of 5 seconds were used. Size analyses were accomplished via mastersizer 2000 equipment, which uses laser diffraction technique to obtain the data. The assays were performed using water as dispersive medium, and ultrasound was turned on for 5 minutes.

2.1 Mixtures composition

The mixtures were prepared with addition of BOFS and GW in order to obtain binary basicity (CaO/SiO_2) of 0.5, 0.9 and 1.2. Table 3 shows the chemical composition obtained via mass balance. The initials MIB means mixtures with basicity index 0.5, 0.9 and 1.2

Elements (%)	% in mass		
	MIB-0.5	MIB-0.9	MIB-1.2
CaO	21.18	30.93	32.02
SiO2	40.0	36.09	26.75
Al203	8.1	7.7	7.11
MgO	7.5	8.7	5.25
MnO	2.6	2.9	3.99
FeO	10.7	9.1	18.44
P_2O_5	1.2	1.2	1.32
C	0.31	0.32	0.32
S	<0.02	<0.02	0.03

Table 3
Mixtures chemical
composition used in the melting process.

2.2 Melting and cooling process

The melting tests were performed at 1500°C for 15 minutes. It was used an InductoTherm induction furnace. Two different cooling were performed. Slowly cooling (into the furnace) was carried out in order to identify phases with indicative of hydraulicity. In this step was used 300 g of each mixture. Fast cooling (in water) was also performed in order to obtain a glassy structure. In this step was used 7 kg of each mixture. X-ray patterns were obtained in both tests to obtain the phases present. Same conditions mentioned previously were used.

3. Results and discussion

3.1 Raw material characterization

X-ray pattern was obtained from BOFS (Figure 1). Basic oxygen furnace slag contain silicate (ranquinite and larnite), which are important to produce Portland cement. It was also noted free calcium oxide (Lime), what is harmful to produce Portland cement. Calcium hydroxide, calcium carbonate, iron oxide and magnesium oxide were also found. Similar compositions were mentioned by Gutt and Nixon (1972) and Motz and Geiseler (2001).

In addition, Figure 2 shows the X-ray pattern from granite waste. X-ray pattern from granite waste showed quartz as mainly components. This suggests a potential to utilization in Portland cement production with BOFS in order to adjust the binary basicity. Quartz is also a vitrifying element, which favor amorphous structure formation. Albite and anorthite, were also detected. Such phases have been detected for several researchers in granite waste composition (Li *et al.*, 2013; Junca *et al.*, 2015).

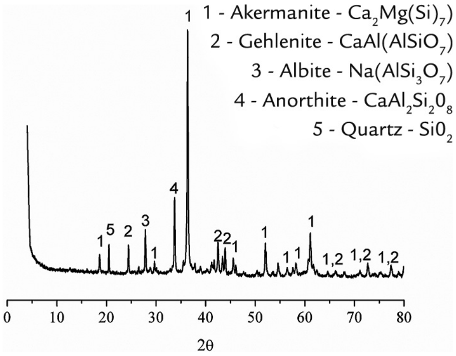

Figure 1
X-ray pattern from
basic oxygen furnace slag.

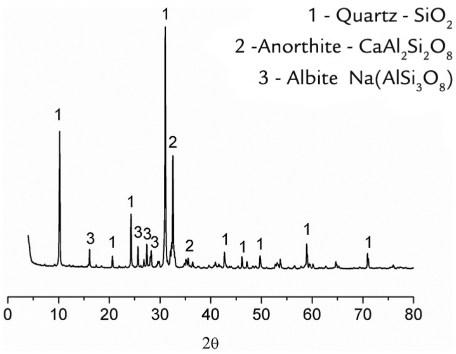

Figure 2
X-ray pattern from granite waste.

Size analysis showed that BOFS is range of 0.479-2187.76 μm, with 90% lesser than 1258.92 μm, and 50% lesser than 478.63 μm. The size analyses from granite waste showed range of 0.414-181.97 μm, with 90% lesser 60.25 μm, and 50% lesser 13.18 μm.

3.2 Molten mixture characterization

Figure 3 shows the X-ray patterns obtained from MIB-0.5, MIB-0.9 and MIB-1.2 slowly cooling into the furnace.

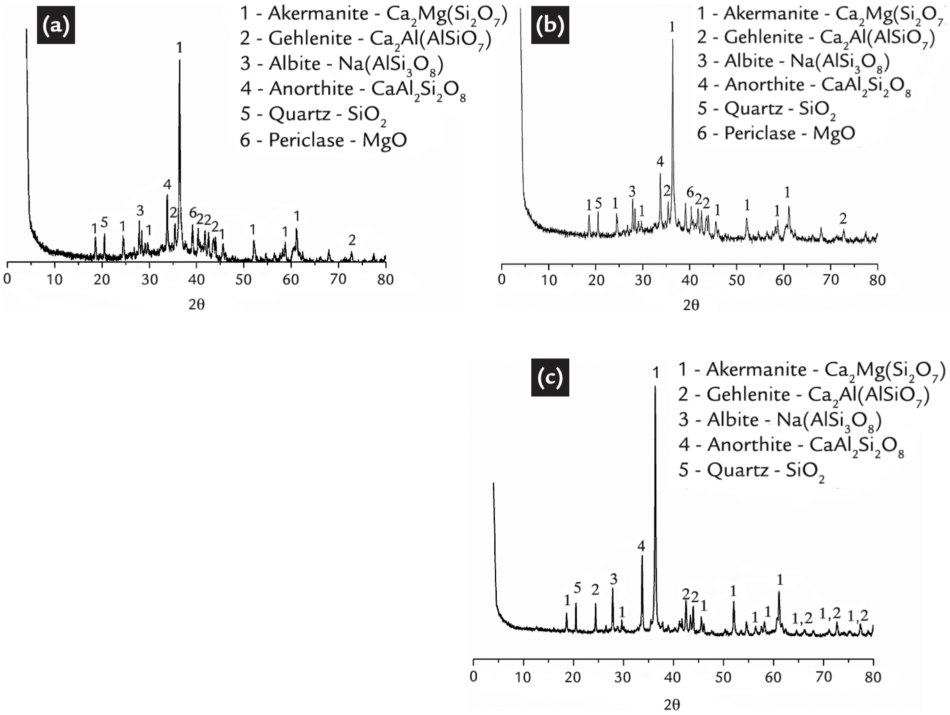

Figure 3
X-ray patterns obtained via slow cooling inside the furnace.
a) MIB-0.5; b) MIB-0.9; c) MIB-1.2.

Addition of granite waste in the BOFS took silicates formation (akermanite and gehlenite). These compounds were not detected in the initial composition in both BOFS and granite waste, which suggests that such phases were formed by chemical composition adequation, i.e. addition of granite waste decreased the mixture binary basicity, which provided the silicates formation. Reduction of unstable oxides (FeO and MgO) and stabilizing oxides dissolution (SiO_2 and Al_2O_3) were also observed.

Figure 4 shows the X-ray patterns obtained via fast cooling in water, which indicates that amorphous structures were obtained in all mixtures.

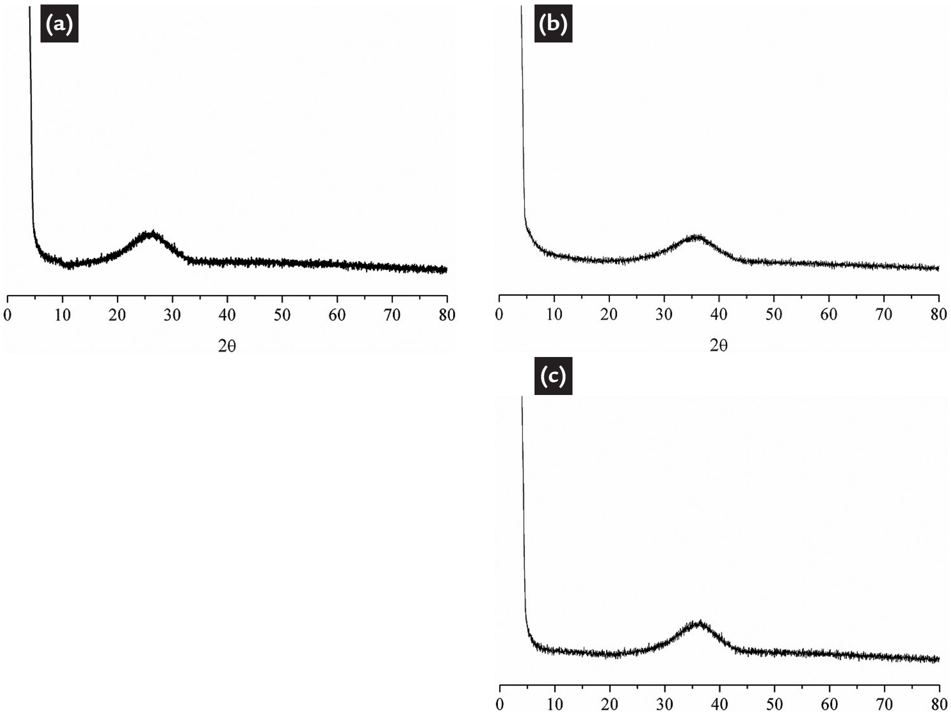

Figure 4
X-ray patterns obtained via fast cooling in water.
a) MIB-0.5; b) MIB-0.9; c) MIB-1.2.

Such fact indicates the formation of silicate glassy structure. According to Smolczyk (1980) and Murphy et al., (1997), formation of glassy structure suggests the possibility to use it in Portland cement production.

Scanning electrons microscope images (Figure 5) showed that glassy structures were formed under fast cooling in water for MIB-0.5, MIB-0.9 and MIB-1.2 mixtures. EDS spectrum also indicates that glassy structures are composed mainly by silicon and calcium, which suggests formation of calcium silicate.

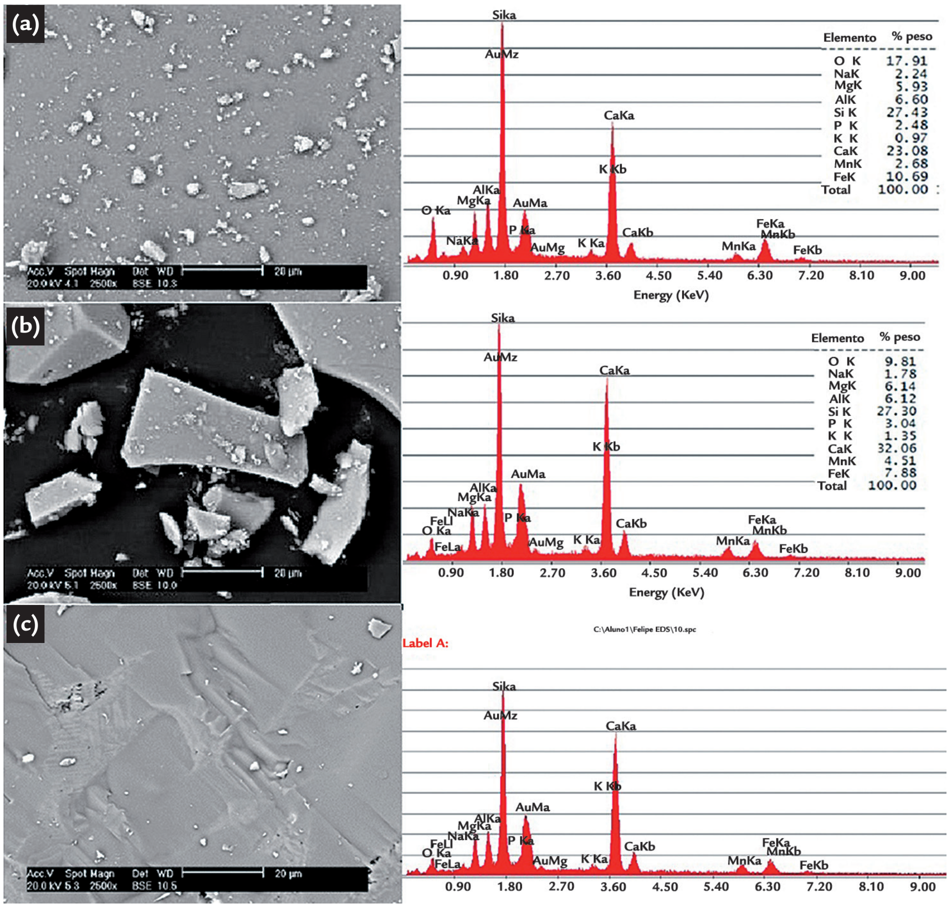

Figure 5
Image obtained via scanning electron microscopy and EDS spectrum to fast cooling in water. a) MIB-0.5; b) MIB-0.9; c) MIB-1.2.

4. Conclusion

Basic oxygen furnace slag showed a higher binary basicity (4.6). It is also composed by silicates (ranquinite and larnite). Granite waste is composed mainly by quartz, and less content of CaO. Mixtures under slowly cooling showed formation of silicates (akermanite and gehlenite). This fact was correlated with chemical composition fit caused by addition of granite waste. Mixtures under fast cooling produced an amorphous structure, as it is also necessary to Portland cement production. Additionally, the fast cooling produced a glassy structure, as it was noted via scanning electrons microscope. EDS spectrum also suggested that glassy structures are formed for calcium silicates. The results obtained indicates a possible utilization of mixtures of granite waste and BOFS to produce Portland cement.

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