The valorisation of acid blast furnace slag (BFS) in supersulfated cements (SSC)

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Abstract

The main purpose of this study was to evaluate the engineering properties of CO_2-free cement made with blast furnace slag (BFS). BFS is a by-product generated in coke or charcoal fuelled steel production. The fact that charcoal comes from a renewable source, eucalyptus, which is planted in large areas of reforestation, is a factor that favours the use of this fuel. However, while BFS produced from coke presents chemical properties that are of interest in Portland cement production, the BFS obtained from charcoal has no similarly useful purpose, which is a growing environmental problem, since charcoal fuelled steel production is increasing. In this study, BFS obtained from charcoal was used as a raw material to produce a CO_2-free cement from supersulfated cements (SSC). The SSC produced contained 85% BFS, 15% calcium sulphate and a small amount of alkali activator. Analysis of the results showed that the SSC made with BFS from charcoal presented a compressive strength lower than the minimum required by EN 15743; however, the engineering properties were acceptable for non-structural applications.
Key-words: charcoal, acid blast furnace slag, by-product, valorisation, supersulfated cements, engineering properties

1 Introduction

Blast furnace slag (BFS) waste generated from the production of pig iron, (which is) a raw material in the production of steel, is widely used around the world. Two types of fuel, coke and charcoal, can be used in the iron melting process. While both are carbon sources, there are basic differences between the processes, including the origins of charcoal and coke. Charcoal comes from the carbonisation of wood with a fixed carbon content (between 56% and 75%), while coke is derived from coal with a fixed carbon content of about 88% (Jacomino et al., 2002). In Brazil, the coke has to be imported due to the poor quality of domestic coal. The fact that charcoal comes from a renewable source, eucalyptus, which is planted in large areas of reforestation, is another factor that favours the use of this fuel. Besides these differences, the type of fuel used during the iron melting process also modifies the chemical characteristics of the slags generated; those generated from coal are usually considered to be basic ($CaO:SiO_2$ ratio > 1), while those generated from charcoal are acid ($CaO:SiO_2$ ratio < 1). Currently in Brazil, the annual production of acid and basic slags are 1.7 and 7.1 million tons, respectively. (Massucato, 2005, Souza Júnior, 2007, Sindifer 2013.) Due to this chemical characteristic, only basic slag is used as raw material in the production of Portland cements. In Brazil, in 2013 alone, cement production reached 71 million tons (SNIC, 2013). In contrast, acid slags have no similarly useful purpose, which is a growing environmental problem, since charcoal fuelled steel production is increasing. Figure 1 presents planted eucalyptus forests and the acid slag produced from charcoal deposited on large patios.

Figure 01: Planted eucalyptus forests (A) and blast furnace slag from charcoal on large patios (B)
Source: Souza Júnior (2007)

The purpose of this paper was to study the valorisation of acid slag in supersulfated cements (SSC) rather than Portland cement. SSC were used in the 1950s and 1960s in Europe, particularly for mass concrete applications. Later, changes in the iron manufacturing processes yielded slags that no longer fulfilled the minimum requirement for Al_2O_3 content (13%), leading to its use in blends with Portland cement (Matschei et al., 2005; Gruskovnjaka et al., 2008, Juenger at al., 2011).

Recently, the standard for SSC in Europe was superseded by the norm EN 15743/2009, which no longer requires a minimum Al_2O_3 content for slag. The requirements now specify that slags "consist of at least two-thirds by mass of the sum of calcium oxide (CaO), magnesium oxide (MgO) and silicon dioxide (SiO_2). The remainder contains aluminium oxide (Al_2O_3) together with small amounts of other compounds. The ratio by mass (CaO + MgO)/(SiO_2) shall exceed 1,0".

In this paper, acid slag was used as a raw material to produce supersulfated cements. Comparisons using a basic slag were also made.

2 Materials and Methods

Two slags, A (acid) and B (basic), were used to produce SSC (Figure 2). Slag A had a CaO/SiO_2 ratio <1 and thus was considered acid, while slag B was considered as basic. Slag A had relatively high amounts of Al_2O_3 and SiO_2 and MgO and lower SiO_2 content; both slags meet the EN 15743 limits (Table 1). X-ray diffraction (XRD) showed that both slags had a glass structure and very similar grain size distribution, both with a d50 of 8 µm (Figure 3).

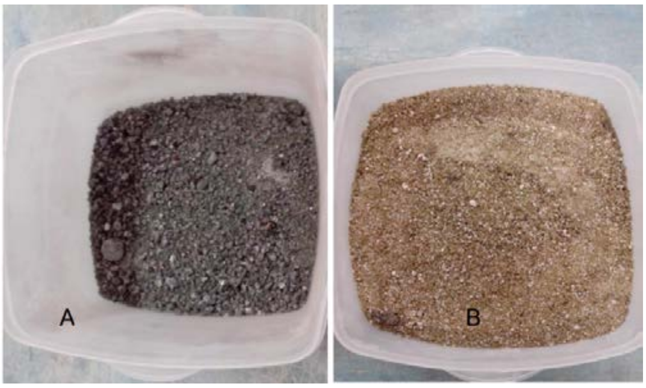

Figure 02: Acid slag (A) and basic slag (B)

Table 1: Chemical composition of acid (A) and basic (B) slag

Oxides	**Slag A**	**Slag B**	**EN 15743**
SiO_2	38.1	32.2	-
Al_2O3	**13.9**	**8.2**	**-**
Fe_2O3	1.3	0.8	-
CaO	37.0	49.5	-
MgO	6.2	5.0	-
SO_3	0.1	1.4	-
Na_2O	0.2	0.1	-
TiO_2	0.8	0.6	-
MnO	1.1	1.3	-
$CaO+MgO+SiO_2$	81.3	86.7	≥66.7
$(CaO+MgO)/SiO_2$	1.1	1.7	≥1.0
CaO/SiO_2	0.97	1.54	-

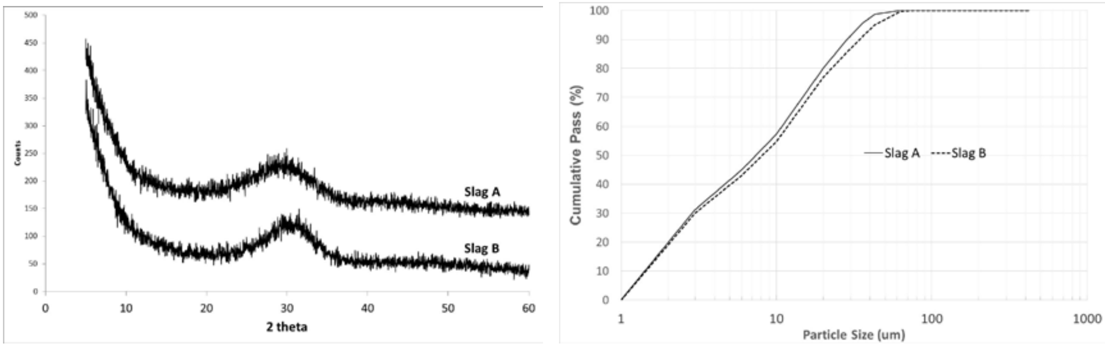

Figure 3: X-Ray diffractogram and particle size distribution of slags A and B used.

The SSC produced contained 85% of slag and 15% of anhydrite as a calcium sulphate source, and potassium and sodium hydroxide were tested as alkali activators.

To obtain anhydrite ($CaSO_4$) for the SSC, gypsum ($CaSO_4.2H_2O$) was burned for 1 h at 650^{o}C and the mineralogical composition was confirmed by XRD (Figure 4).

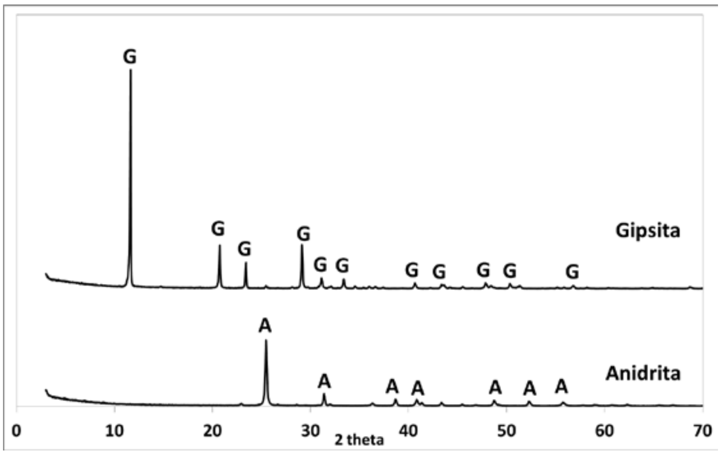

Figure 4: X-Ray diffractograms of gypsum (G) and anhydrite (A).

The compositions of the SSC are presented in Table 2.

Table 02: Compositions of the SSC (%)

Slag	BFS	CS	KOH	NaOH
Acid slag (A)	85	15	2, 5 , 8	5
Basic Slag (B)	85	15	0.5	-

The compressive strength of mortar was determined (cement:sand:water 1:2.75:0.485) at 7 and 28 days, cured in sealed plastic bags.

Pastes with a w/c ratio of 0.4 were prepared. Using a TamAir isothermal calorimeter, heat evolution measurements were determined for 20 g of SSC over a hydration period of 7 days at 23^{o}C. For XRD analysis, these pastes were cured in saturated limewater solution and at 7 days were crushed into particles smaller than 9.5 mm, immersed in acetone for 2 h and dried by filtration to remove the pore fluid. These dried samples were crushed again to obtain particles smaller than 75 µm. These powders were then submitted to X-ray diffraction analysis using CuKα radiation, over a 2θ range of 3°–70°, using steps of 0.02° and 10 s counting time.

3 Results and Discussions

The mechanical performance of the SSC made with acid slag (A) containing KOH (2, 5 and 8%) and NaOH (5%) is presented in Figure 5. A mortar produced with basic slag, using KOH as an activator, was also fabricated for comparison.

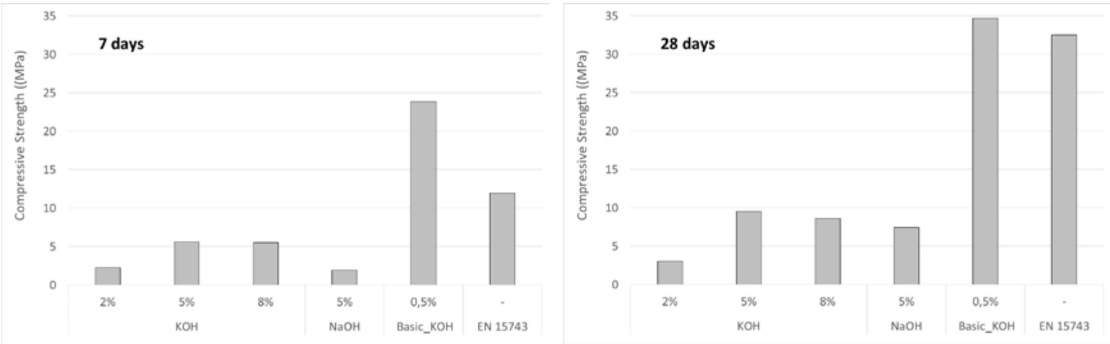

Figure 5: Compressive strength of mortar of SSC made with acid slag (2, 5 and 8%) and basic slag (0.5%) containing KOH and NaOH as activator

Slag A required much more activator content than slag B and its compressive strength was significantly lower than slag B at 7 and 28 days. The values presented by the two activators were similar, but KOH was slightly better. SSC made with 5% KOH presented the highest value, but it still did not achieve the minimum requirements of EN 16743 (32.5 MPa), in contrast with basic slag.

Figure 6 presents the total heat in pastes made with acid slag (5% KOH and NaOH) and basic slag (0.5% KOH) up to 7 days.

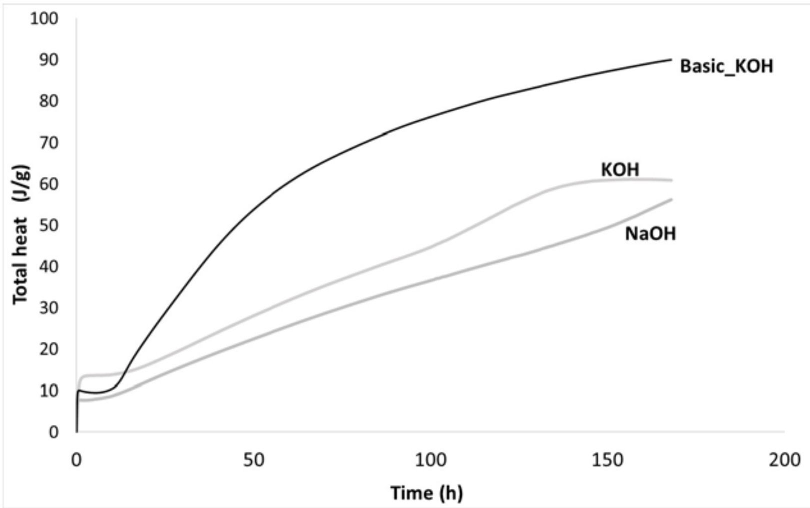

Figure 6: Isothermal calorimetric measurements: heat flow rate and total heat release of pastes with acid slag containing 5% of KOH and NaOH up to 7 days.

The curves confirmed the results obtained for compressive strength, showing that the hydration reactions were more intense for basic slag; for acid slag, KOH provided greater heat release, confirming the higher compressive strength results.

The XRD analysis showed that SSC made with acid slag presented ettringite and gypsum as the main hydration phases, which were also observed in basic slag. KOH provided a higher dissolution of anhydrite in relation to NaOH, but the formation of ettringite was very similar. However, the formation of gypsum was significantly higher for NaOH and it seemed to have a negative effect on the mechanical performance (Figure 7).

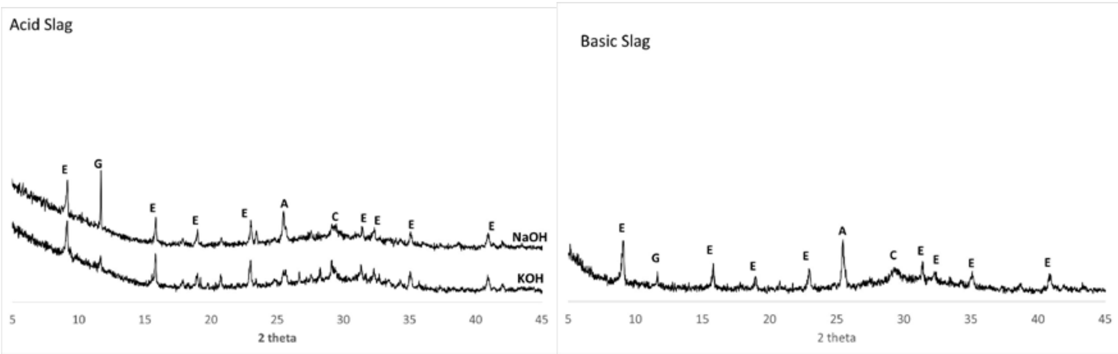

Figure 7: X-Ray diffractograms of pastes with acid slag containing 5% of KOH and NaOH and with basic slag containing 0.5% of KOH at 7 days

E: ettringite, G: gypsum, A: anhydrite, C: calcite

4 Conclusions

Analysis of the results obtained showed the performance of SSC made with basic slag was significantly higher than those made with acid slag. The compressive strength tests showed that the amount of activator content (KOH) required was much greater for acid slag; however, the XRD analysis showed that the main hydration products were presented in SSC made with acid slag.

Although the results obtained showed a compressive strength lower than the minimum value required by EN 15743, SSC made with acid slag also presented interesting results. A compressive strength of 12 MPa would allow its use as coating mortars and concrete block, which are widely used in masonry in Brazil.

The possibility of producing SSC with acid slag represents a very important environmental contribution for the process of charcoal fuelled steel production.

Given the large production of cement in Brazil, this is one way that acid slag residue can be used, contributing to cement production free from CO_2 emissions and at lower energy costs.

Acknowledgements

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