Proceedings Paper:

Bernal Lopez, S. orcid.org/0000-0002-9647-3106, Ke, X., Hussein, O. et al. (1 more author) (Accepted: 2016) Effect of testing condition on the loss on ignition results of anhydrous granulated blast furnace slags determined via thermogravimetry. In: Segment on Concrete with Supplementary Cementitious Materials. International RILEM Conference on Materials, Systems and Structures in Civil Engineering (MSSCE), 21-24 Aug 2016, Lyngby, Denmark. PRO113 - Proceedings of the International RILEM conference Materials, Systems and Structures in Civil Engineering, segment on Concrete with Supplementary Cementitious Materials . RILEM Publications S.A.R.L. , Lyngby, Denmark , p. 299. ISBN 978-2-35158-178-0

Full citation: PRO 113 – Proceedings of the International RILEM Conference on Materials, Systems and Structures in Civil Engineering Conference - Segment on Concrete with Supplementary Cementitious Materials 22-24 August 2016, Technical University of Denmark, Lyngby, Denmark (ISBN 978-2-35158-180-3, e-ISBN 978-2-35158-181-0), p. 299-307

International RILEM Conference on Materials, Systems and Structures in Civil Engineering
Conference segment on Concrete with Supplementary Cementitious Materials
22-24 August 2016, Technical University of Denmark, Lyngby, Denmark

EFFECT OF TESTING CONDITIONS ON THE LOSS ON IGNITION RESULTS OF ANHYDROUS GRANULATED BLAST FURNACE SLAGS DETERMINED VIA THERMOGRAVIMETRY

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Abstract

A key property influencing the quality of a blast furnace slag (GBFS) used in cements and concretes is the loss on ignition (LOI), which is associated with the amount of moisture and carbonates present. Both EN and ASTM standards describe determination of the LOI of GBFS, and thermogravimetric analysis (TGA) is also a valuable test which provides information that can be related to the LOI. However, the final mass loss obtained by TGA is influenced by the testing conditions including nature and flowrate of the gas used, the sample mass and heating rate, and there is no existing standard method for TGA of SCMs. As part of the efforts of RILEM TC 238-SCM, this study assesses the effect of the gas environment and gas flowrate on the observed mass loss from a GBFS, determined via TGA in nitrogen, argon or air atmospheres using different gas flowrates, and without correction for oxidation of sulfides to sulfates. Significant mass changes occur between 800–1000 °C independent of the gas used, and are more notable under an oxidising atmosphere and at low gas flowrates. These results elucidate that it is required to standardise TGA testing parameters for analysis of GBFS to enable collection of meaningful results by this technique.

1. Introduction

Most modern concretes contain supplementary cementitious materials (SCMs) such as granulated blast furnace slag (GBFS), a by-product derived from the iron making industry, as partial replacements of Portland cement. The growing interest in the utilisation of SCMs is mainly associated with their environmental benefits, and the enhanced performance developed by blended concretes, compared with those without additions [1, 2]. However, as some SCMs are wastes or by-products from different industrial practices, it is imperative to ensure their accurate physical and chemical characterisation to determine suitability for use as building materials. One of the tests used to assess the quality of slags is the loss on ignition (LOI), used to identify pre-hydration or weathering which can affect slag reactivity and thus impact the performance of the concretes produced. The LOI of GBFS can be determined according to the standardised testing method EN 196-2 [3] which specifies to ignite the sample in an oxidising atmosphere at 950 ± 25 °C to assure that the carbonates and water present in the sample are completely removed, and that oxidation of any iron, manganese or sulfides takes place. Similarly, ASTM C114 [4] specifies to ignite the sample at 950 ± 50 °C. In both standards the procedure to correct the LOI values due oxidation of sulfides is specified.

Thermogravimetric analysis (TGA) of construction materials including gypsum [5] and fly ashes [6] has been identified as a faster method for determination of mass loss upon heating. However, results from TGA are strongly influenced by the testing conditions such as the geometry of the cell and balance, the nature and flowrate of the gas environment used, the amount of sample tested, and the heating rate used, among other parameters. As there is no existing standardised method for TGA of SCMs, variation among different laboratories are identified, which can lead to misleading results regarding the quality of a given SCM.

As part of the efforts of working group 1 (WG1) of RILEM TC 238 SCM, the present study assesses the effect of the nature and flowrate of the gas environment on the measured mass loss of a blast furnace slag, as determined via TGA coupled with mass spectrometry. Anhydrous slag samples were tested in nitrogen, argon and air atmospheres using gas flowrates of 20, 40, 60 and 100 mL/min. Complementary in-situ heating X-ray diffraction of the slag was conducted in air, to elucidate potential formation of crystalline solid reaction products via the interactions of sulfate species forming in the slag at high temperatures.

2. Experimental programme

2.1. Material and tests conducted

An anhydrous GBFS supplied by RILEM TC 238-SCM, whose chemical composition is shown in Table 1, was used in this study. Its loss on ignition, determined according to BS EN 196-2, was 0.84%

Table 1. Chemical composition of the GBFS as determined by X-ray fluorescence. The entry reported as “SO$_3$” is the oxide equivalent of the total sulfur content, which was determined to be present 8.5% as sulfate and 91.5% as sulfide. Data provided by RILEM TC 238-SCM.

	Al_2O_3	**SiO_2**	**CaO**	**MgO**	**Fe_2O_3**	**“SO_3”**	**Na_2O**	**K_2O**
wt.%	11.59	36.45	40.78	7.45	1.4	2.1	0.5	

TGA of all samples was carried out in a Perkin Elmer TGA 4000 instrument coupled with a Hiden mass spectrometer. 40 mg of sample was tested from 30^{o}C to 1000^{o}C at a heating rate of 10^{o}C/min. Commercial-grade argon, nitrogen or air were used as sample purge gases, at varying flowrates between 20 and 100 mL/min.

To determine the potential formation of sulfate-rich phases upon heating of the GBFS, in-situ heating X-ray diffraction (XRD) experiments were carried out in a D5000 Siemens diffractometer with Cu-Kα radiation and a nickel filter. Samples were heated from room temperature to 1050 °C at a heating rate of 10 °C/min. Measurements were taken at room temperature before heating, 750 °C, 850 °C, 950 °C, 1050 °C during heating, and 30 °C after cooling down from 1050 °C. The XRD scans were acquired with a step size of 0.02° and a counting time of 2 s/step from 5° to 55° (2θ). The temperature was held constant while each diffractogram was collected.

3. Results and discussion

3.1. Thermogravimetric analysis

Fig 1 shows significant differences in the thermograms as a function of the type of gas and the gas flowrate used. Between 30°C and 200°C only minor mass changes were identified in all the samples, independent of the testing conditions. Notable differences in the mass loss were observed between 200°C and 650°C depending on the type of gas used. For samples tested in argon (Fig 1A), at gas flowrates between 20 and 60 mL/min minor differences were detected; however, an increased rate of gas flow (100 mL/min) led to a higher mass loss within this range of temperatures than was observed at lower gas flowrates. When using nitrogen (Fig 1B), an increased mass loss was observed at lower gas flowrates, although no significant differences in the mass loss were identified when using 40 and 60 mL/min of gas. Variations in the mass loss were not observed in this range of temperatures when testing the samples in air.

The most significant mass changes observed under all testing conditions took place between 650°C and 1000°C, a temperature range of significant relevance when comparing to determination of LOI according to different standard methods. For samples tested in argon (Fig 1A) at gas flowrates below 60 mL/min, a slight mass gain is observed between 650°C and 930°C, followed by a significant increase in mass up to 1000°C. This was more notable in the samples tested at the lower gas flowrates. Conversely, using 100 mL/min of argon induced a slight mass reduction at higher temperatures of testing. Comparable results were identified for samples tested in nitrogen (Fig 1B), however, greater mass loss is observed at higher gas flowrates. In samples tested under 60 and 100 mL/min of nitrogen, mass gains above 900°C were not identified. It appears likely that these mass increases in the presence of lower flowrates of ‘non-oxidising’ gases may be related to the insufficient purging of oxygen from the furnace – whether entering due to improper furnace sealing, released from the slag in mass loss processes then reabsorbed at higher temperature, or from other sources – but confirmation of this theory would require further investigation using a broader range of slags and other specimens.

For specimens tested in air (Fig 1C), a two stage mass gain is observed, independent of the gas flowrate used. The first mass gain took place between 650°C and 930°C, and the second from 930°C to 1000°C. There is a clear consistency in the ranges of temperatures at which the mass gain was observed across the different testing conditions, not just for samples tested in air, but also for samples tested in argon and nitrogen. This indicates that similar phenomena are governing the mass gain of this GBFS at high temperatures, independent of the gas and flowrate used during testing. All of the TGA tests showed a maximum mass loss at a temperature just below 700°C, reaching a value of around 1% which was significantly greater than the measured LOI of the slag.

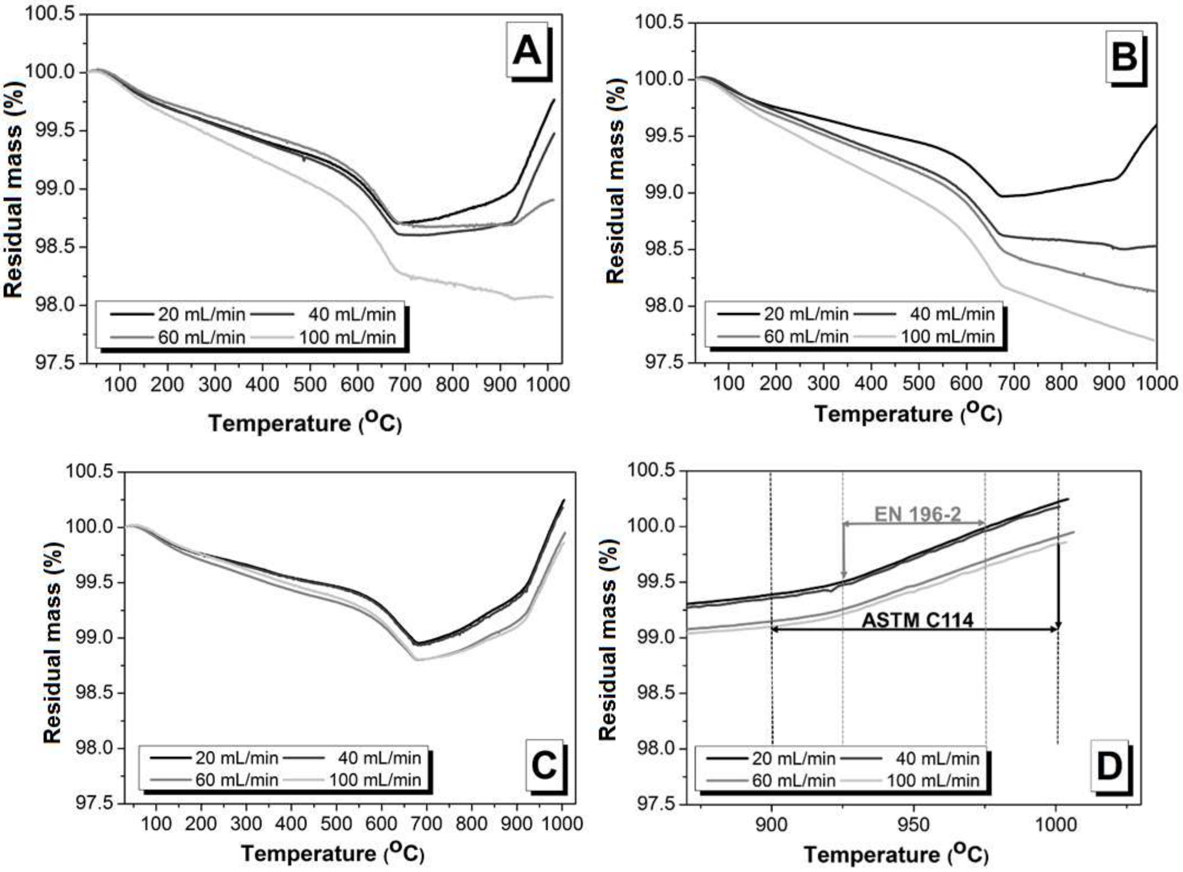

Fig 1. TGA results, as a function of the gas flowrate, of anhydrous GBFS tested under (A) argon, (B) nitrogen and (C) air at flowrates as marked, and (D) enlargement of the thermograms in air, highlighting ranges of temperatures used to determine LOI in EN and ASTM standards

The mass loss values of the slag at 950°C determined by TGA (uncorrected for any mass gain due to oxidative reactions) are reported in Table 2, where it can be seen that the type of gas and the gas flowrate used during testing strongly influence the measurements. For all gases used, a high gas flowrate gives an increase in the mass loss. Slight differences were identified in the mass loss values obtained when using nitrogen or argon at the different gas flowrates; however, when using air (which is specified as the gas environment in the standardised LOI tests), the mass loss values were four to five times lower than the values obtained when using nitrogen or argon, due to the oxidative processes taking place in the presence of this gas atmosphere. The temperature at which the mass loss is determined influences significantly the measured mass change, as shown in Fig 1D, and this variability is greater when adopting the range of temperatures recommended by ASTM compared with that stipulated in the EN standard. In conducting that LOI test, the absolute change in mass recorded at 950°C was in fact a gain of 0.31%, with the application of the EN 196-2 sulfide oxidation correction (subtraction of 1.15%

in this case) yielding the underlying loss value of 0.84%. This value is within the range of the results obtained when testing the slag in air and using a gas flowrate higher than 60mL/min (Table 2).

Table 2. Mass loss at 950°C of the anhydrous GBFS determined by TGA*

Type of gas	**Gas flowrate (mL/min)** **20**	**40**	**60**	**100**
Argon	0.83 ± 0.23	1.07 ± 0.22	1.25 ± 0.08	1.94 ± 0.01
Nitrogen	0.68 ± 0.16	1.49 ± 0.01	1.83 ± 0.02	2.25 ± 0.03
Air	0.26 ± 0.24	0.29 ± 0.24	0.53 ± 0.22	0.59 ± 0.21

***** Range of the residual weights (%) obtained at 950 ± 25°C; no correction for sulfide oxidation applied

3.2. Mass spectrometry

Fig 2 shows the measurement of the evolution of oxygen concentration during TGA of a GBFS, as a function of the gas type and flowrate. When using Ar or N_2 as purging gases, a significant reduction in O_2 was observed with an increase in the gas flowrate. In both of these cases negligible contents of O_2 were detected when using gas flowrates of 60 and 100 mL/min. Therefore, it is unlikely that mass changes under these testing conditions are associated with oxidation reactions of reduced species in the GBFS. However, at lower flowrates (20 and 40 mL/min argon, 40 mL/min nitrogen), a sharp dip in O_2 concentration is observed at 900°C, which corresponds closely to the sharp increase in mass in Fig.1 in these samples, and thus provides further weight to the identification of this mass increase as being related to an oxidative process. Conversely, negligible changes in O_2 concentrations are identified when using air as the purge gas, between the different gas flowrates assessed, where the oxygen content of the purge gas is registered in the mass spectrometer.

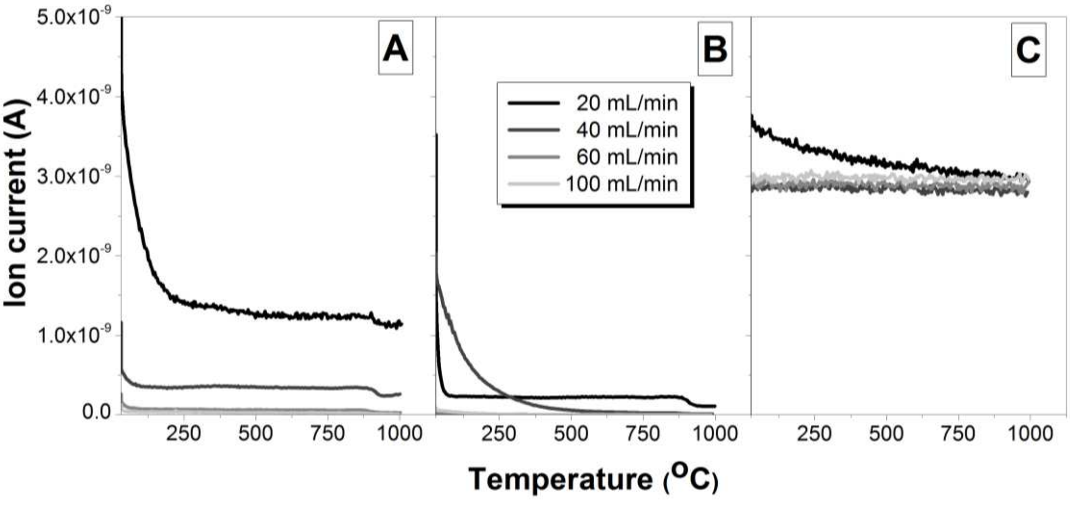

Fig 2. Mass spectra of $O_{2(g)}$ detected during TGA of an anhydrous GBFS when using (A) argon, (B) nitrogen or (C) air, as protective gases

Fig 3 shows mass spectroscopy measurements of $H_2S(g)$ and $SO_2(g)$ during heating of samples tested using a low gas flowrate (20 mL/min). When using an N_2 gas environment, $H_2S(g)$ is the predominant sulfur-containing gas up to 800°C. At higher temperatures, a significant drop in the concentration of this gas is observed, consistent with the increase in SO_2(g) concentration. Similar results were identified when using dry air, where an initially low concentration of H_2S(g) was detected at temperatures below 200°C, followed by a significant increase in its concentration at temperatures between 200 and 800 °C. This elucidates that at temperatures relevant for LOI determination the complete oxidation of sulfide has not taken place, even when testing GBFS in air.

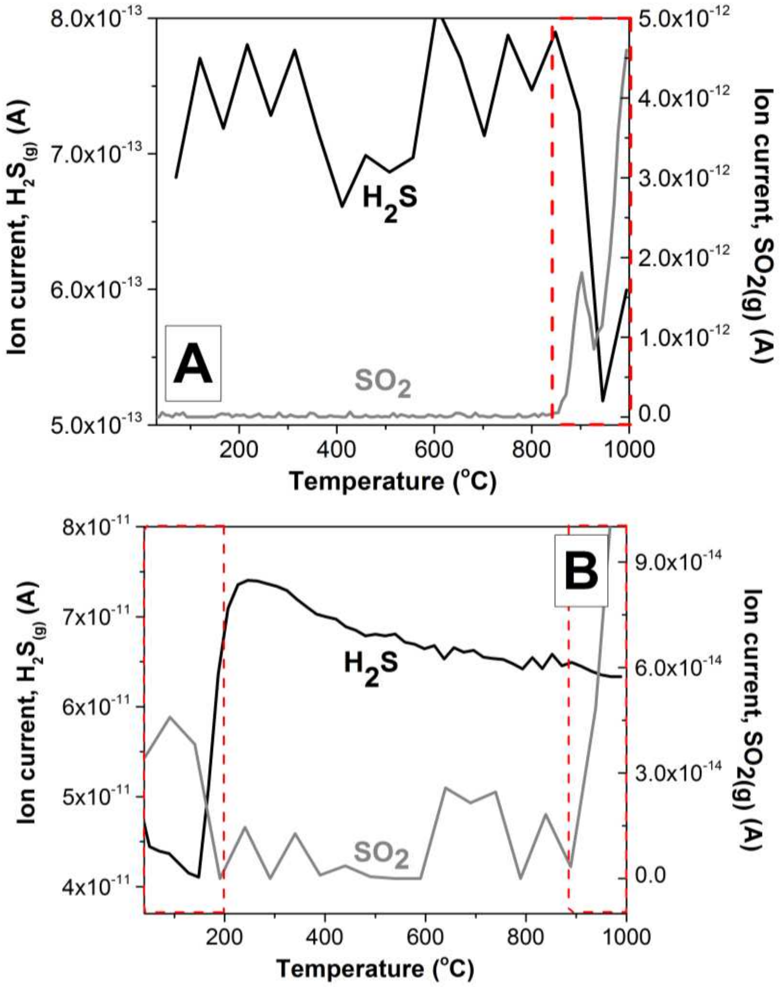

Fig 3. Mass spectroscopy results for H_2S(g) and SO_2(g) detected during TGA of anhydrous GBFS using 40mg of sample, and 20 mL/min of (A) N_2 or (B) air

The mass spectroscopy results for H_2O(g) and CO_2(g) (Fig 4) indicate that the mass losses observed in the thermograms below 700°C (Fig 1) correspond to dehydration (between 30°C to 500°C) and decarbonation (between 250°C to 700°C) of the GBFS. Independent of the type of gas and the gas flowrate used, these reactions took place in the same temperature ranges.

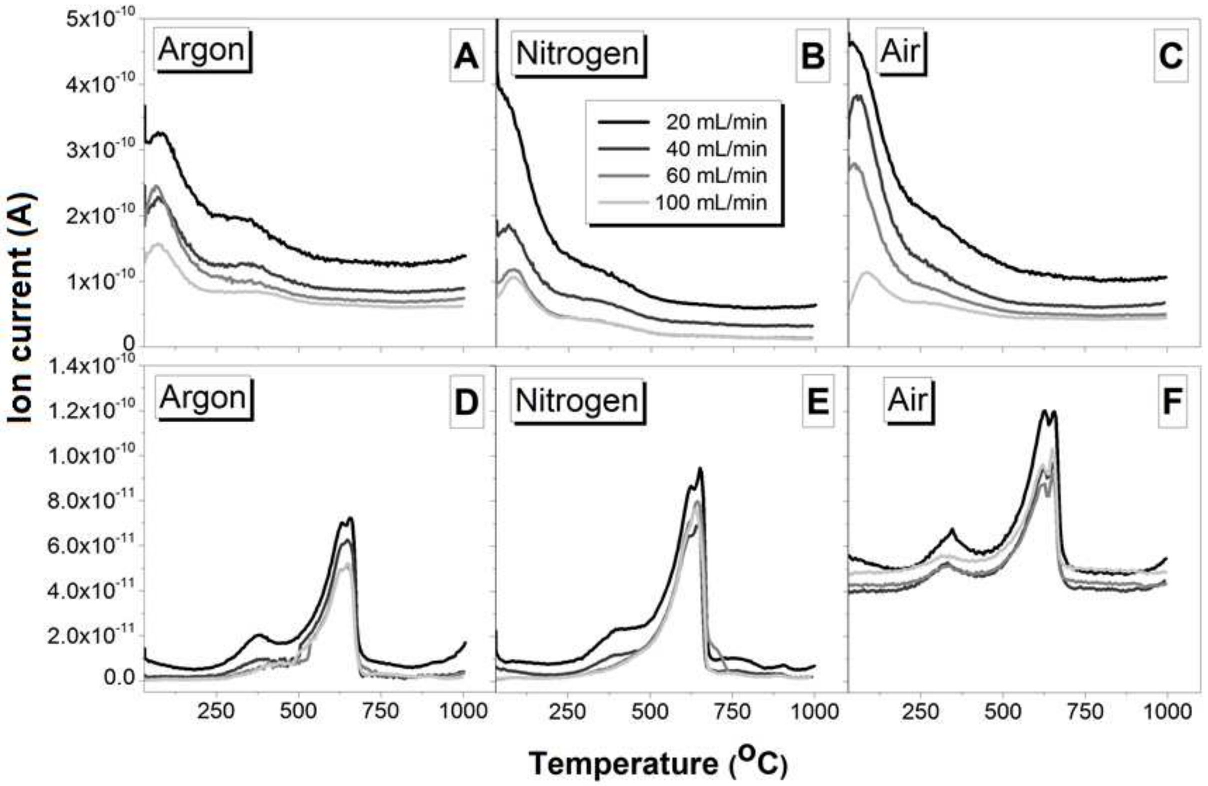

Fig 4. Mass spectroscopy results for $H_2O_{(g)}$ (A, B, C) and $CO_{2(g)}$ (D, E, F) detected during TGA of an anhydrous GBFS, as a function of the gas environment

For all the testing conditions assessed, an increased gas flowrate reduced the concentration of $H_2O_{(g)}$ released from the GBFS. Only minor differences in the concentration of CO_2 were identified as a function of the gas flowrate, indicating that the decomposition of carbonates present in the GBFS is not affected significantly by the nature of the gas environment used during TGA. Hence, the nature of gas and its flowrate during TGA of GBFS have a negligible effect on the quantified amounts of carbonates.

3.3. In-situ heating XRD

Fig 5, presenting X-ray diffractograms collected in situ during heating of GBFS in air, shows that GBFS crystallisation starts taking place between 850°C and 950°C and involves the formation of a transient phase wollastonite-2M ($CaSiO_3$, powder diffraction file (PDF) #43-1460), followed by the formation of åkermanite ($Ca_2MgSi_2O_7$, PDF# 35-0592), as well as another polymorph of monocalcium silicate ($CaSiO_3$, PDF# 34-0612) and kilchoanite ($Ca_6(SiO_4)(Si_3O_{10})$, PDF# 46-1479).

Formation of sulfur-rich crystalline phases was not identified; however, the range of temperatures at which crystallisation of the GBFS was identified is consistent with the second mass gain observed by TGA (Fig 1), corresponding to the oxidation of S^{2-} species (Fig 5). This indicates that the structural changes taking place in the GBFS glass at the point of crystallisation are also increasing the mobility of sulfur-containing species, because the capacity of the glass to host sulfides is much greater than its potential degree of incorporation into any of the crystalline phases identified in Fig 5.

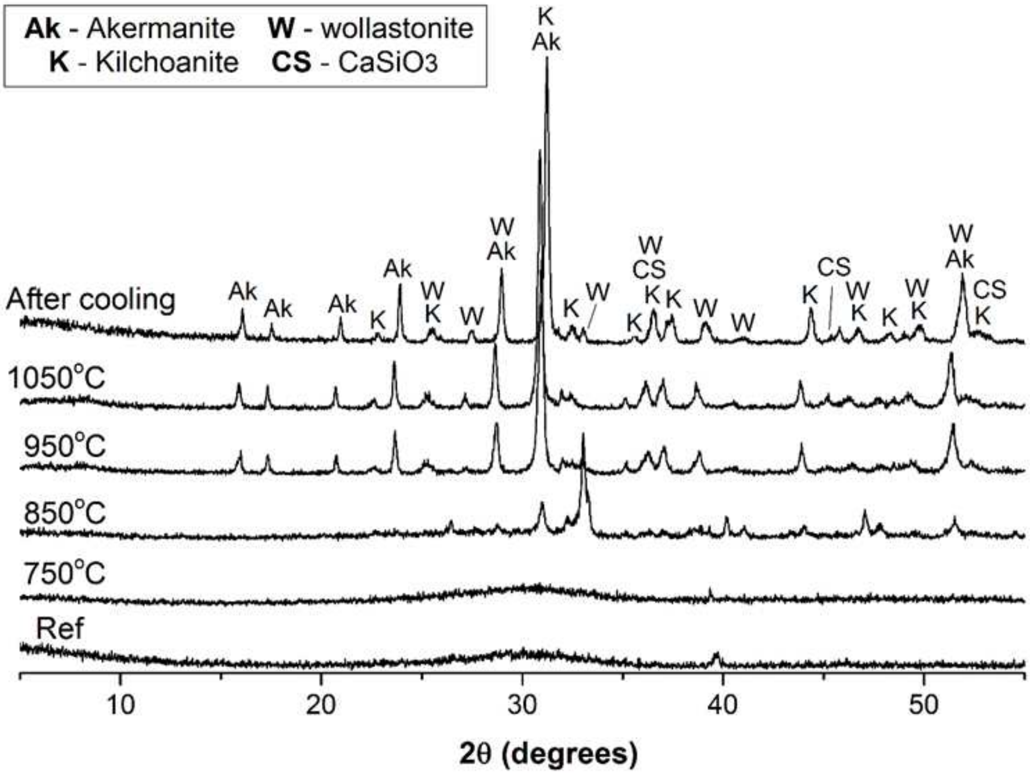

Fig 5. In-situ heating X-ray diffractograms (Cu Kα radiation) of an anhydrous GBFS

4. Conclusion

This study provides evidence that the testing conditions adopted during TGA for characterisation of SCMs, such as GBFS, strongly influence the ability to determine mass loss, and thus potentially to calculate LOI values, from those data. Therefore, the application of this technique needs to be standardised so that samples are evaluated under similar TGA testing conditions, and results for different slags across different laboratories can be compared. It is noted that a limitation of this study has been that the small sample masses studied (40 mg in each case) precluded the accurate measurement of sulfate content of the slags after heating, and so the corrections for oxidation of sulfide to sulfate which are specified in standard LOI determinations could not be implemented.

Upon heating the GBFS undergoes three main process (i) the removal of evaporable water (30°C - 500°C), (ii) decomposition of carbonate species (300°C -750°C), and (iii) oxidation of sulfides (>750°C). The mass changes associated with each of these reactions depend on the type of gas and gas flowrate used during testing. When the ‘inert’ gases argon or nitrogen were used, a minimum gas flowrate of 60 mL/min (approximately double the usual recommended flowrate for this instrument) was required to eliminate oxygen gas and consequently hindered the mass gains associated with the oxidation of the sulfides present in the GBFS. If determination of pre-hydration and/or weathering of the slag is desirable, it may be recommended to conduct LOI analysis at 750°C to minimise the convoluting effects of higher-temperature oxidation processes, which appear also to be linked to the onset of slag glass devitrification as identified by XRD.

The gas flowrate does not have a significant impact on the measured mass loss in an air environment, hence comparable results are obtained over a wide range of gas flowrates, although the mass loss values were up to three times lower than those reported when using nitrogen or argon as protective gases. The temperature selected to determine the LOI, within the allowable variation in standard test methods, may significantly affect the results obtained as the main mass changes in GBFS are observed between 900°C and 1000°C. Considering the high sensitivity of TGA, it is recommended to specify a narrower range of temperatures to determine LOI, than is stipulated in the EN and ASTM standards, to reduce variability of LOI results across laboratories.

5. Acknowledgments

This research was funded by the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) / ERC Grant Agreement #335928 (GeopolyConc). The authors thank all members of RILEM TC 238-SCM for valuable discussions, in particular M.C.G Juenger (U. Texas at Austin, USA) and B. Lothenbach (EMPA, Switzerland) for their insight during the planning of these experiments. We thank Sam Walling (U. Sheffield) for the determination of LOI of the slag.

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