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The determination of low levels of crystalline silica in slag and silica fume

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Abstract

The determination of low levels of the quartz form of crystalline silica in ferrous slags and silica fume samples was carried out using differential scanning calorimetry (DSC). Such quantitative information is required for the classification of these and other cementitious materials according to the Workplace Hazardous Materials Information System (WHMIS) and other environmental as well as health and safety provisions. The International Agency for Research on Cancer (IARC) now requires Materials Safety Data Sheets for products containing 0.1% or more crystalline silica. A calibration curve correlating the quartz content with the height of the endothermic peak of the α/β quartz polymorphic transformation was constructed using the standard addition method. The technique and the methodology were found to be reliable and convenient, and enabled the detection of quartz levels below 0.1% in the samples. © 1997 Elsevier Science B.V.

Keywords: Crystalline silica; DSC; Quartz; Silica fume; Slag

1. Introduction

With the steady increase in the environmental awareness and the rapid development of more stringent regulations, the demand for more sensitive analytical techniques for the detection of trace amounts of undesirable contaminants has significantly increased. The detection of low levels of crystalline silica in slags and silica fume is required for the classification of these materials according to the Workplace Hazardous Materials Information System (WHMIS). Quartz is by far the most common form of crystalline silica. Information on the determination of the quartz content of clays and other materials using differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are found in the literature [1,2]. In an earlier publication by Rowse and Jepson [1], a detailed comparison between DTA, X-ray diffraction and chemical analysis techniques for this application was reported. They concluded that DTA was the superior method, proving the best experimental precision. In a more recent publication by Norton [2], 5% quartz in an alumina matrix was easily quantified by DSC. Norton also examined the main factors affecting the quality of data and level of detection and further predicted detection levels of <1% quartz in certain mixtures by this technique. In the present work, DSC was used in an attempt to attain the lowest possible level of detection for quartz in ferrous slag and silica fume.

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2. Materials and experimental procedure

Four different samples of iron-making blast furnace slag and a sample of silica fume were used in this investigation. The samples were suspected to contain trace amounts of quartz. A TA 2100 thermal analysis system with a differential scanning calorimeter module DSC 910 was used. Optimum conditions for maximum sensitivity were developed to allow the lowest possible detection limit of quartz using the capabilities of the equipment. A DSC cell constant of 2.0, a N_2-purge rate of 50 ml/min, a data sampling interval of 0.2 s/data point, a sensitivity of 1X and a heating rate of 20°C/min were used in the experiments. The samples and reference material (α-Al_2O_3) were contained in crimped aluminium pans. The DSC temperature calibration was done using indium and quartz standard reference materials. Attempts were made to keep a constant sample size in all experiments to avoid errors due to potential non-linear signal dependency on sample size.

3. Methodology

The method of standard addition was used in this work. The method involves the development of a calibration curve based on the measurement of heat flow obtained as a result of the α/β polymorphic transformation of quartz around 573±3°C. In the preliminary work, a slag sample that did not show any detectable peak at ~573°C was chosen as a matrix for the quartz additions. Six mixtures were prepared by adding known amounts, namely, 0.1, 0.2, 0.5, 1, 2, and 4%, of high-purity quartz to the matrix sample. The quartz was an NBS - ICTA Standard Reference Material #760 with 99% purity and ~100 μm particle size. A high-sensitivity Mettler balance (±0.1 μg) was used in the preparation of the mixtures. The conformity of the experimental data to the expected linear relationship between the transformation peak height and the quartz content of the slag was established.

4. Results and discussion

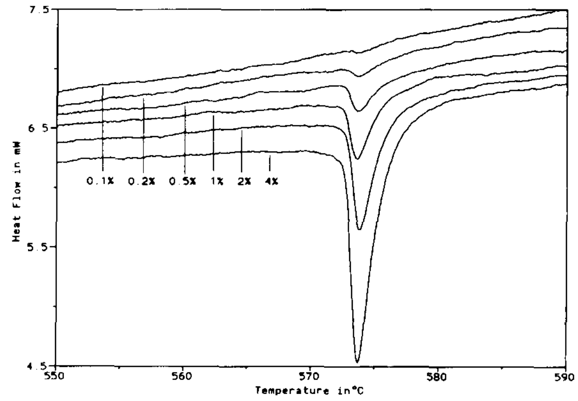

Fig. 1. DSC curves of six different mixtures of quartz in a slag matrix.

Fig. 1 shows DSC curves of the six different mixtures of quartz and matrix slag. It can be seen in Fig. 1 that the peak obtained for 0.1% sample approaches the limit of detection of the equipment. Different methods of data treatment were used, namely, peak area and peak height with linear and sigmoidal baseline. Best results were obtained by measuring the peak height with a linear baseline. Fig. 2 represents the linear relationship between the quartz content of the slag matrix and the quartz transformation peak height. This calibration line is based on a sample size of 30 mg.

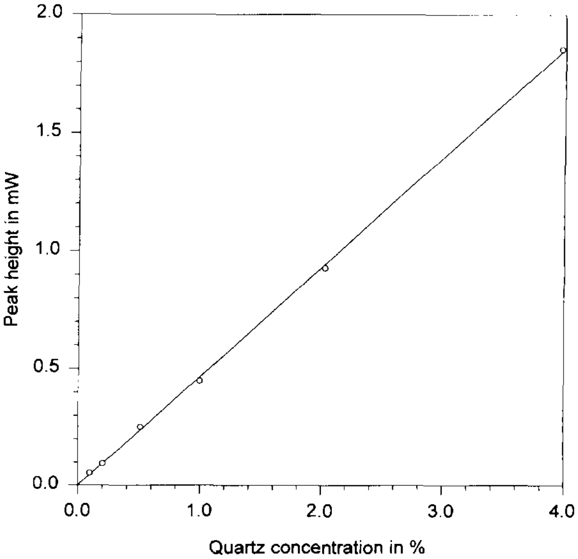

Fig. 2. A correlation between the quartz content of the slag matrix and the peak height (calibration line).

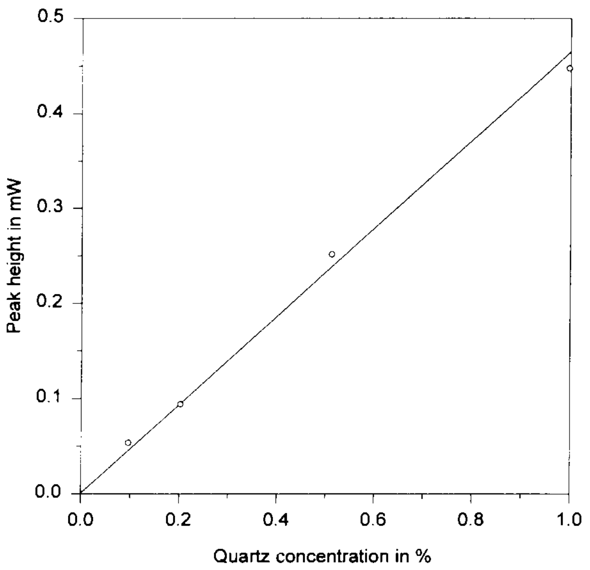

Fig. 3. An expanded scale of the calibration line shown in Fig. 2.

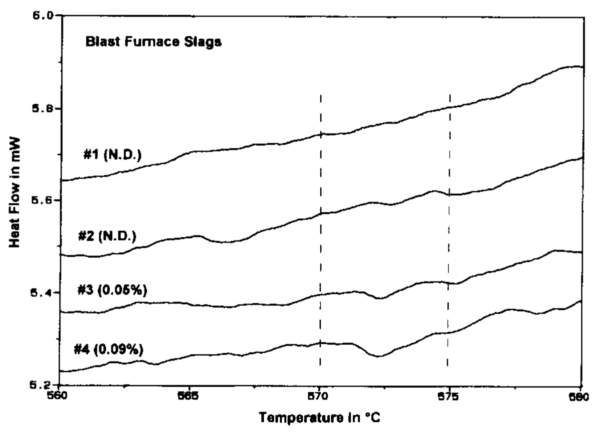

Fig. 4. DSC curves of four slag samples including the matrix sample.

The slope of the line is 0.4644, the correlation coefficient is 0.99967 and the intercept is 0.0007717. The calculated deviation from the origin (the x-axis intercept), representing the unknown amount of quartz in the matrix slag, was insignificant (0.0017%). The selection of this particular sample as a matrix for the standard quartz additions was therefore justifiable. Fig. 3 is an expanded scale (0–1%) of Fig. 2, verifying the conformity of the experimental data to the linear relationship at this lower range.

Fig. 4 shows the DSC curves of the four slag samples, including the matrix sample. By using the same data treatment method, namely peak height with a linear baseline, the quartz content of the four samples was determined as undetected, undetected 0.05 ± 0.03% and 0.09 ± 0.02%, for samples 1–4, respectively. The estimated range of error was based on the repeatability and standard deviation of the prepared mixtures from the calibration line at the lower range (< 0.1% quartz).

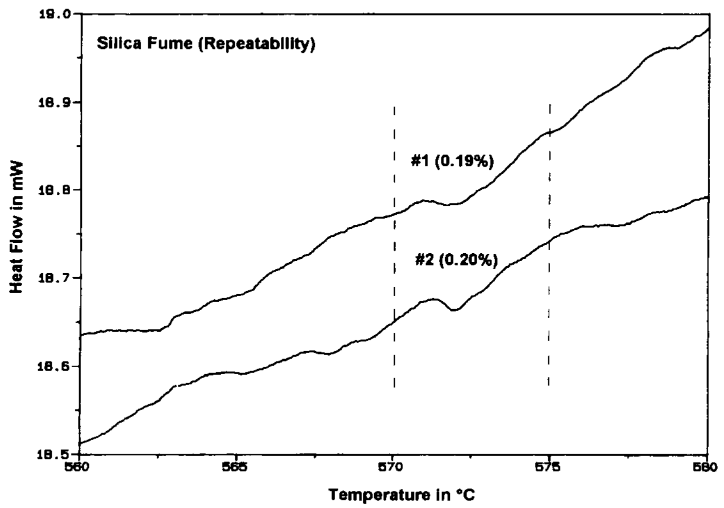

Fig. 5. DSC curves of the silica fume sample and a repeat.

Fig. 5 shows the DSC curve of the silica fume sample and a repeat. The calibration line for the slag was also applied to the silica fume; although, ideally, silica fume should have been used as a matrix but only one sample was available. Moreover, only 10 mg samples were used in the case of silica fume. Fig. 5, therefore, was only included to demonstrate the feasibility of measuring low levels of quartz in a silica fume matrix and the repeatability of the measurements. A slight smoothing of the data was also done in this case. The results of the two experiments were 0.19% and 0.20% quartz, respectively, indicating an excellent repeatability in this range.

Potential sources of error in the technique may include sample handling, weighing and mixing of very small amounts of materials, grinding which may lead to the formation of amorphous silica, large variation in the particle size of the sample and that of the pure quartz used in the standard addition, and the presence of impurities with thermal activities in the same temperature range as that of the polymorphic transformation of quartz.

5. Conclusions

1. DSC is a fast, reliable and convenient technique for the determination of low levels of the quartz form of crystalline silica (<0.1%) in ferrous slags and silica fume. At present, this seems to be the only technique capable of such determinations in bulk materials.
2. Data treatment using peak height with a linear baseline seems to produce the best correlation with the quartz content. With the optimization of experimental parameters, a linear relationship between the quartz content and the DSC peak height and a correlation coefficient as high as 0.99967 is achievable.

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