

Lab Report XRD 65

Quantitative phase analysis of Blast Furnace Slag Cements

Introduction

Granulated ground blast furnace slag (GGBFS) is a major constituent of CEM II/A-S, CEM II/B-S and CEM III cements. Blast furnace slag is a predominantly amorphous product, containing small amounts of crystalline phases like Akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), Merwinite ($\text{Ca}_3\text{MgSi}_2\text{O}_8$), or Quartz (SiO_2). It offers hydraulic properties similar to those of Portland Cement and hence may partly substitute the clinker component in cement blends.

Obviously clinker burning is a main source of CO_2 emissions. Therefore blast furnace slag cements are increasingly produced in order to reduce cement making specific CO_2 emissions.

Quality assurance and surveillance requires the determination of the main constituents of the finalized cement. Current regulations allow several methods to estimate the slag content in cements, such as gravity separation (ENV 196-4:1993), selective dissolution (ENV 196-4:1993), microscopic analysis (DIN 1164-1:1990) or the determination based on the chemical composition. These methods are either time consuming, require special laboratory work, or pre-knowledge about the sample.

This Lab Report demonstrates how the analysis of amorphous phases can be seamlessly integrated into the TOPAS Rietveld calculation without further need for calibration or adding a standard.

Rietveld Quantification of amorphous phases

By definition, traditional Rietveld analysis takes only crystalline phases into account. The relative weight fractions are normalized to 100 wt. %. Amorphous amounts can only be determined indirectly by adding a known weight fraction of an internal standard to the sample (also called the "spiking method").

In an automated process laboratory this method can hardly be realized. Furthermore, systematic errors can arise from microabsorption effects due to differences in mass absorption of sample and standard. Accurate analysis using the spiking method requires similar mass absorption and grain size distribution of both sample and standard.

In contrast to traditional Rietveld TOPAS allows the consideration of phases with partially or no known crystal structure in the calculation (PONKCS [1]) by using `hkl_Phases` (Pawley or Le Bail fitting).

Quantitative phase analysis applying such models requires an empirical "calibration" step, because of lacking structure information. The mass of such phase is not known. To do a proper calibration, samples of known composition are mandatory to define the mass accordingly.

PONKCS: Quantitative Rietveld analysis of phases with partially or no known crystal structure

The weight fraction w_i of the i -th phase in Rietveld analysis is defined by:

- the scaling parameter s_i ,
- the volume V_i of the unit cell.
- the weight of the atoms $M_i Z_i$ (M = Mass of one formula unit, Z = number of formula units in cell) inside the unit cell and

$$w_i = \frac{s_i \cdot V_i \cdot M_i \cdot Z_i}{\sum_{j=1}^n s_j \cdot V_j \cdot M_j \cdot Z_j}$$

Rietveld quantification using hkl_Phases instead of structures:

- Using hkl_Phases the intensity values are derived from a measurement of the peak intensities.
- If an hkl_Phase is used in quantitative Rietveld analysis, only the volume V of the unit cell is known.
- Rietveld quantification requires the “calibration” of the Mass (MZ) of the hkl_Phase, because of the lack of structural information.

$$w_i = \frac{s_i \cdot V_i \cdot \underbrace{M_i \cdot Z_i}_{\text{needs to be calibrated}}}{\sum_{j=1}^n s_j \cdot V_j \cdot M_j \cdot Z_j}$$

Experimental Setup

The measurements were executed using a D4 ENDEAVOR diffractometer in Bragg-Brentano Geometry equipped with the 1-dimensional LynxEye™ compound silicon strip detector (fig. 1). The settings are given in Table 1. The quantitative phase analysis was done using the DIFFRAC^{plus} TOPAS (Version 4) software.

Table 1: D4 ENDEAVOR configuration with the LynxEye Detector

| | |
|------------------------|---|
| Goniometer | D4 ENDEAVOR Theta/2Theta |
| Measurement circle | 401 mm |
| Tube | 2.2 kW Cu long fine focus |
| Tube power | 35 kV / 50 mA |
| Primary optics | Divergence slit fixed to 0.5° 4° Soller slit |
| Sample stage | Rotating sample holder |
| Secondary optics | Nickel K β Filter 4° Soller slit |
| Detector | LynxEye (opening 3.9°) |
| Step size | 0.02° |
| time per step | 0.2 s |
| angular range (2Theta) | 10° to 65° |
| Total Measuring time | 9 min 50 sec |

Samples

In 2006, the VDZ (German Cement Works Association) organized a round robin on quantitative phase analysis of blast furnace slag cements using XRD methods.

A set of samples was distributed to the participants to be analyzed. This set comprised three Slag Cements of different compositions. The preliminary published outcomes [2] provided the reference values of the slag amounts in each cement sample (table 2).

Table 2: Composition of the Slag Cement Samples used in the VDZ Round Robin

| Sample No. | Sample description | Slag Content in wt. % |
|------------|---------------------------|-----------------------|
| 1 | CEM II/B-S | 25 |
| 2 | CEM III/B 32,5 N-NW/HS/NA | 67 |
| 3 | CEM III/B 42,5 N-NW/HS/NA | 72 |



Figure 1: The 1-dimensional LynxEye compound silicon strip detector.

Sample Preparation

10 grams of each sample were ground in an automatic preparation unit POLAB®APM, using Polysius tablets as binder. The samples were pressed in steel rings.

Setup of the hkl_Phase model to describe the blast furnace slag

The modeling of the amorphous diffraction data is realized by the following steps:

- Measurement of the pure blast furnace slag
- Whole Powder Pattern Decomposition of the amorphous intensities by Pawley fitting using an arbitrary start model
- Empirical „calibration“ of the mass (MZ) of this model to meet the results of the reference samples

This approach results in a perfect description of the amorphous diffraction characteristics as shown in figure 2.

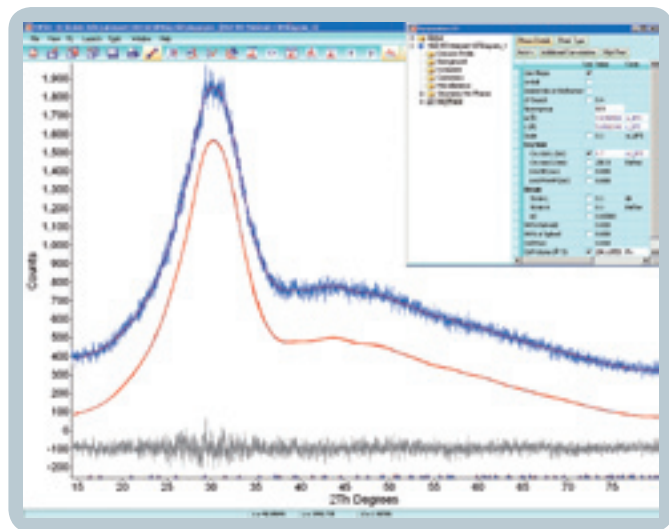


Figure 2: Structureless modelling of amorphous blast furnace slag. The blue curve represents the measured data. The calculated model is represented by the red curve. The difference is plotted in grey.

Results

All three round robin samples were quantified using the same hkl_Phase model for calculating the blast furnace slag. The repeatability of measurement was investigated by analyzing each sample five times. For each of the runs the sample was unloaded and reloaded to the diffractometer. Figure 3 shows measurement data of round robin sample 1 and the TOPAS quantification result.

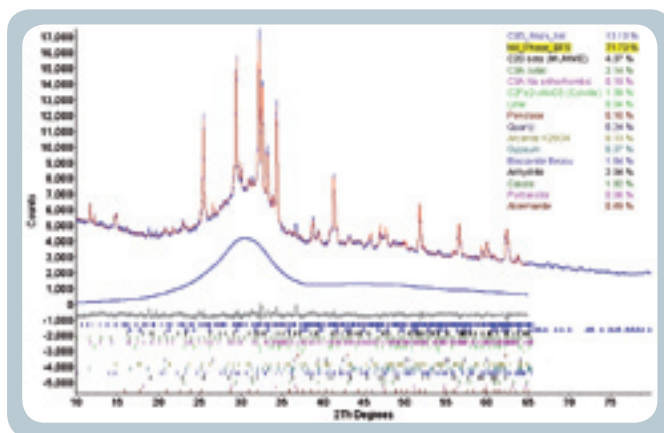


Figure 3: Measurement result (blue) and TOPAS calculation (red) of Slag Cement sample 1. The difference of both is given in grey. The marks indicate the peak positions of each phase with a known structure. The blue curve above the difference curve indicates the intensity contribution of the amorphous blast furnace slag.

Table 3: TOPAS quantitative phase analysis of the VDZ round robin slag cement samples (values given in wt.%)

| | Sample 1 | Sample 2 | Sample 3 |
|------------------|-------------|-------------|-------------|
| Measurement 1 | 25.0 | 67.2 | 71.7 |
| Measurement 2 | 25.1 | 67.3 | 71.9 |
| Measurement 3 | 24.7 | 67.0 | 71.6 |
| Measurement 4 | 25.1 | 67.3 | 71.9 |
| Measurement 5 | 25.3 | 67.0 | 71.5 |
| Mean | 25.1 | 67.2 | 71.7 |
| Std. Dev. | 0.2 | 0.2 | 0.2 |

The TOPAS PONKCS method provided accurate results (Table 2 and 3) covering a broad range of slag concentration. The repeatability was significantly better than known from existing methods currently established. The absolute standard deviation of the calculated slag concentrations was 0.2 wt. %.

Note: In this study, predominantly amorphous blast furnace slags were analyzed. The analysis can be easily extended to slag qualities showing a larger degree of crystallinity, by simply adding additional crystalline phases to the TOPAS calculation. No further work is required.

Conclusion

TOPAS defined a new generation of Rietveld analysis through the fundamental parameters approach [3]. Its unrivalled performance for quantitative phase analysis is based on powerful minimization algorithm, mathematical stability, and unmatched speed of calculation. Another sophisticated feature is demonstrated in this Lab Report.

By adding PONKCS a remarkable extension of quantitative analysis capabilities of TOPAS is realized. Seamlessly integrated into fully automated Rietveld analysis TOPAS' PONKCS enables blast furnace slag quantification with outstanding accuracy, precision, and

reliability. By using modern detector technology, like the ultra fast Compound Silicon Strip Detector LynxEye, results can be obtained within minutes.

The benefits of the PONKCS method are manifold. It is easy to implement as there is no calibration at the plant level required. It is independent of tube aging. Compared to existing reference methods the analysis is fast, operator independent and frees up your valuable personnel resources for more specialized tasks. The speed of measurement allows the implementation of this analysis not only for quality assurance and surveillance, but also for process control.

Keywords

XRD, quantitative phase analysis, TOPAS, Blast Furnace Slag Cements, Pawley fitting, PONKCS

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