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Crystalline silica in pellets

Rietveld-XRD analysis for REACH classification

Author(s):

Sieger R van der Laan

Corus Research, Development & Technology

IJmuiden Technology Centre

CRC

Address code 3J22

PO Box 10.000

1970 CA IJmuiden

The Netherlands

T 0251-492901



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Summary

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Rietveld-XRD analysis for REACH classification

Author(s): Sieger R van der Laan
Reviewer(s): Stefan Melzer
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For purpose of REACH classification 10 different pellet samples have been presented to Corus-CRC for Crystalline Silica analysis using X-ray diffraction and the Rietveld method for quantification of measured patterns. A second set of the same samples has been presented to the Centro de Tecnologia de Ferrosos of Vale to perform the same analysis.

In this report the findings of Corus – CRC are presented.

Customer: CSPY-EM-C&P
Programme manager: Jan Bottema

Approved by:

Corus Research, Development & Technology
IJmuiden Technology Centre
CRC
Address code 3J22
PO Box 10.000
1970 CA IJmuiden
The Netherlands

Crystalline silica in pellets

1. Introduction

For purpose of REACH classification the crystalline silica (CS) content was determined of ten different pellets commonly used in European Blast Furnaces as produced by various suppliers. Analyses were performed by two laboratories, the Ceramics Research Centre of Corus RD&T at IJmuiden, The Netherlands, and the Centro de Tecnologia de Ferrosos of Vale SA at NOVA LIMA – MG, Brazil.

Total silica content as determined in chemical analysis (e.g., XRF) is not necessarily indicative of CS content. Basicity plays a role – e.g., silica in pellets can also be present in other phases, most commonly olivine. Therefore the different pellets have been tested for total CS content by XRD analysis.

In addition to bulk CS in pellets, the respirable CS fraction in pellet dust is of interest. Although standardised tests are used in minerals industry to generate dust (CEM standard), we opted for separating the adhered dust fraction from two pellet samples to compare this to the bulk CS value.

2. Materials and Methods

Ten samples of one kg of representative material were presented to the CRC lab for analysis. Pellets were crushed and a sub-sample was grinded to analytical fine using a tungsten-carbide ball mill. Samples were analysed by X-ray Diffraction.

Technical details of the analytical methodology were harmonized between the Corus and VALE laboratories. We considered the request to "analyse pellets for Crystalline Silica contents" as a determination of mineral contents of the pellet sample. We agreed to only report Crystalline Silica and not the other constituent minerals. The way we would go about the analysis has been verified with the Iron Platform which requested the analysis.

The procedure both labs will apply therefore is:

- crushing of a representative subsample of pellets followed by grinding of a representative subsample of the crushed pellet material.
At Corus:
 - grinding under cyclohexane in a small ball mill producing about 5 g of powder of appropriate grainsize for Quantitative -powder XRD
 - mix-in 10wt% of Si-metal as internal standard, using a Retch Schnellmuehle
- XRD-patterns will be taken from 10-130 degree 2theta
At Corus:
 - stepsize 0.02 degree 2theta and dwell time of 1 sec. per step
 - with a Co-tube 35kV 45mA.
 - using a Bruker D4 powder diffractometer with a Vantec detector
- Patterns will be evaluated for minerals present, and then quantified using the Rietveld method
At Corus:
 - using TOPAS Bruker software.
- Only reported are crystalline silica phases and their wt% presence in the bulk pellet sample.

3. Results

3.1 CS in bulk pellets

The results as obtained at the CRC lab of Corus, are presented in Table 3.1.1 and in Figure 3.1.1 and 3.1.2. We report Quartz, cristobalite and tridymite contents in wt% as well as total CS, the sum of all CS. Given error margins represent 2 sigma confidence limits and are further clarified in section 3.3. The total CS content of pellets ranges from below detection limit (less than 0.5 wt% total CS) up to 5.3 wt%. Three samples contain no CS, meaning they have values below detection limit. In three samples quartz is predominant at 2-3 wt%, in two samples it is tridymite at about 1 wt%.

Table 3.1.1: Crystalline Silica content of 10 pellet samples as determined with XRD-Rietveld method

	JSCMGOK	JSCMGOR	AS08	AF08	1e bedinsky GOK	Peña pellets MH2188	KPBA pellets	MPBO pellets	San Marco Low Si	Castillo de San Jorge
	2σ	2σ	2σ	2σ	2σ	2σ	2σ	2σ	2σ	2σ
Quartz (SiO ₂)	3.0	1.2	1.7	0.1	2.2	0.6	0.3	0.0	0.0	0.0
Cristobalite (SiO ₂)	1.6	0.9	0.4	0.0	0.9	0.8	0.2	0.1	0.1	0.0
Tridymite (SiO ₂)	0.7	1.1	0.5	0.2	0.5	0.2	0.9	1.0	0.0	0.0
total CS	5.3	3.2	2.4	0.4	3.6	1.6	1.4	1.1	0.1	0.0

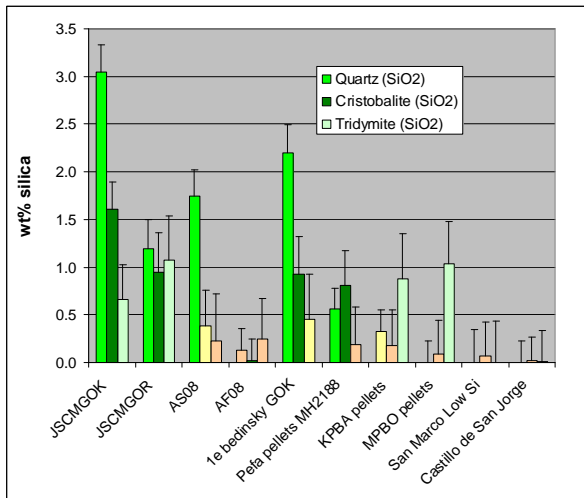
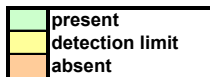


Fig. 3.1.1: CS contents of 10 pellet samples with 2σ error, values at detection limit are in yellow, below detection in orange.

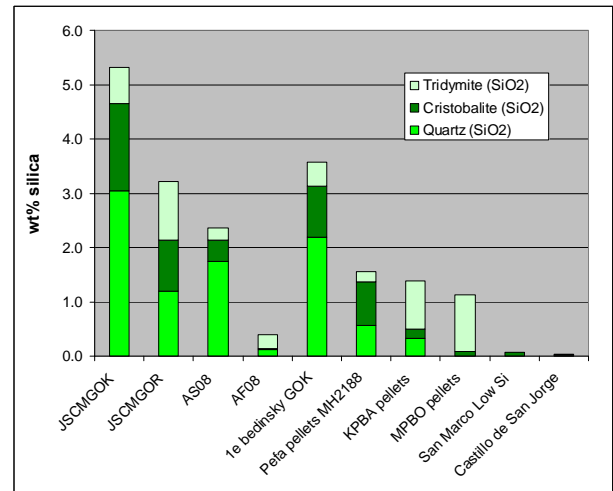


Fig. 3.1.2: total CS content of 10 pellet samples.

3.2 CS in dust adhered to pellets

All sample material, as delivered, contained small amounts of dust. The dust was separated of two samples to obtain an impression of respirable CS associated with pellets. Coarse screening with a 4mm – 0.5 mm sieve stack was followed by microsieving to obtain the dust fraction 10-20 micron and smaller than 10 micron. All dust which passed the 10 micron sieve was filtered over a 0.3 µm milipore filter, effectively yielding a 0.3-10 micron dust fraction. For one sample it was noticed that a lot of material stayed in suspension, this was decanted and separately passed through a milipore filter. With the help of SEM the grainsize of the suspension material was established as 0.3-5 micron. It should be noticed that the amount of dust associated with the pellets is very low, and the obtained fraction smaller than 20 micron is only about 0.5 gram out of a total of 1 kg of pellet sample.

Results of XRD-Rietveld analysis on the two pellet dust samples are presented in Table 3.2.2 and Figure 3.2.1 and 3.2.2. Of one sample we report values for the 10-20 micron as well as the 0.3-10 micron dust fractions. Of the other sample we report the 0.3-10 micron fraction which settled out of the water column, and the 0.3- 5 micron fraction obtained as suspension. The dust samples contain more CS than the bulk samples. Especially the suspension sample is enriched in CS compared to the bulk. It is well known that minerals of lower density need more time to settle than those of higher density. Preferential extraction of CS is therefore expected to occur when separating a fraction in suspension.

Table 3.2.1: CS in dust fraction of pellets.

	JSCMGOK 0.3-10 µm		JSCMGOK 10-20 µm		PEFA 0.3-5 µm suspension		PEFA 0.3-10 µm		
Quartz (SiO ₂)	4.2	0.5	6.1	0.6	1.9	0.9	1.0	0.5	present
Cristobalite (SiO ₂)	1.8	0.4	1.9	0.4	1.2	0.7	0.5	0.4	detection limit
Tridymite (SiO ₂)	0.7	0.8	0.6	0.8	2.1	1.5	0.3	0.9	absent
total CS	6.6	1.1	8.5	1.1	5.2	1.9	1.9	1.1	

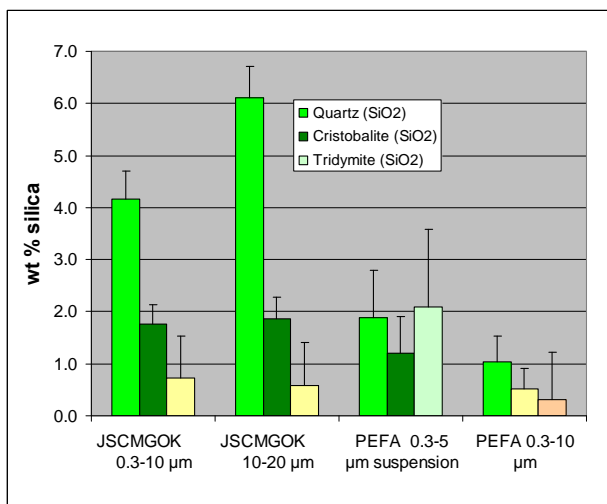


Fig. 3.2.1: CS contents of 2 pellet dust samples with 2σ error, values at detection limit are in yellow, below detection in orange.

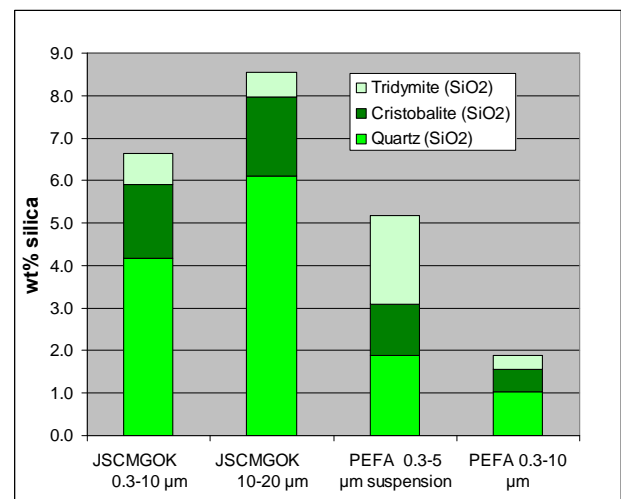


Fig. 3.2.2: total CS content of 2 pellet dust samples. Two grainsize fractions reported per sample.

3.3 Explanation to the reported error margin of analysis

An explanation regarding the reported errors has been requested and is given in this section. For Corus CRC the 2 sigma error on CS in the pellet data is:

For quartz: 0.2-0.3 wt%

For cristobalite: 0.3-0.4 wt%

For tridymite: 0.3-0.5 wt%

The error margin on total CS was calculated using the standard statistical method for error propagation (error in sum equals square root of the sum of squared individual errors).

The given error (2 sigma) of analysis on a single crystalline silica phase is the minimum possible error arising from random errors (statistics). This includes also errors due to model inadequacies. Thus, phase proportions will randomly scatter within this statistical error for each new Rietveld fit of the measurement, especially when new phases are added. Phase proportions below the statistical errors are not reliable. The errors are therefore also the detection limits.

These random fluctuations in the model fit have caused some earlier release to deviate somewhat from the current reported values of the Corus –CRC Rietveld results, but note that previous values are identical to current values within the reported error margins.

Rietveld analysis is a full pattern fitting technique for X-ray diffraction data. Many factors are of importance regarding the error margins of Rietveld analysis. When intensities of reflections for a mineral are close to background, the background fit has some influence on outcome of the Rietveld analysis. The quality of the XRD apparatus and the duration of measurement influence the detection limits. Given detection limits are for Corus – CRC standard acquisition times of XRD patterns. With longer measurement this will improve. Particularly with older XRD apparatus, or detectors, data may be worse, and consequently detection limits and errors are worse. Different laboratories will tend to get different results on the same samples, but within given error margins results should agree.

4. Appendix: Example of Rietveld fit to XRD-pattern - Corus CRC

