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HERZOG

Impact of sample preparation using various disc mills on the within-lab repeatability of XRF analysis

Abstract

Variability of the grinding process within disc mills may impact particle grain size and consequently impair the repeatability of X-ray fluorescence (XRF) analysis of cement samples. Accordingly, the use of two different disc mills within one laboratory possibly causes an increased analytical variability if the grinding process in both machines is not completely uniform. In this application note, we assessed the repeatability of XRF analysis of ten CEM II/A-LL 42,5 R cement samples after preparation on two different disc mills of the HP-MP type. The tests were carried out under the everyday conditions of the laboratory of a large German cement plant. In each HP-MP we found an excellent repeatability of XRF results. Comparison of both HP-MP revealed perfectly congruent results with only negligible differences for some elements. Acceleration data from both disc mills revealed highly reproducible and uniform grinding processes ensuring the high within-lab repeatability found in this study.

Key words

• **Repeatability** • **XRF analysis** • **Sample preparation** • **Cement** • **Laboratory**

Introduction

X-ray fluorescence (XRF) is an analytical method frequently used in many different industrial applications. Due to its high accuracy and short latency until result, XRF analysis is frequently used in the quality control of cement production. However, the intensity of analytical lines can be influenced by various factors including, e.g., absorption, mineralogical variation, and particle size.

Proper sample preparation is essential to achieve reproducible and accurate XRF results. Especially, minimizing the variability of particle size distribution is important as even a small decrease in the grain size may lead to a significant increase in the intensity [1, 2]. In most QC laboratories of the cement industry, disc mills are used for grinding of samples of cement and different precursor materials like, e.g., raw meal and clinker. Therefore, a good reproducibility of the disc grinding process is an important prerequisite for a high precision of XRF results.

In larger cement plants, two or more disc mills are usually required to handle and prepare the high number of samples sent to the laboratory.

Accordingly, a high reproducibility of the grinding process is not only mandatory within one disc mill machine but also among the various machines used in the laboratory.

In this application note, we aim at investigating the effect of using different disc mills on the precision of XRF analysis. For this purpose, we prepared cement samples using two different combined milling and pelletizing machines of the HP-MP type and analyzed them on the same XRF analyzer. The study was carried out under the realistic everyday conditions of a quality control laboratory of a large German cement plant.

Methods

The tests were carried out in the fully automated laboratory of a German cement plant. The laboratory has been installed about six months before running the analyses. The automation consists of two pneumatic airtube laboratory stations (type HR-LA, Herzog, Germany), three combined milling and pelletizing machines (type HP-MP, Herzog, Germany), two granulometers, two x-ray fluorescence (XRF) spectrometers, and two diffractometers (Figure 1). All machines were linked to each other by conveyor belts transporting the sample cups and pressed pellets between the automation components and analyzers.

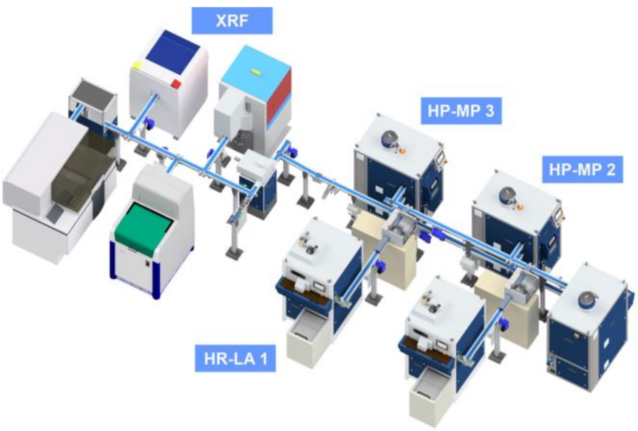

Figure 1: *This graph displays the layout of the quality control laboratory of a German cement plant. The samples are pneumatically sent within air tube carriers from the plant to the laboratory. The carrier arrive in the laboratory station HR-LA where there are unpacked and dosed into cups which are then transported to the HP-MP for sample preparation.*

In this study, we compared the influence of sample preparation using either HP-MP 2 or HP-MP 3 on the XRF analysis of CEM II/A-LL 42,5 R cement. The third HP-MP within this laboratory was excluded from this study as it was mainly used for special material requiring special sample preparation parameters and pressing tools.

Before the test, the cement material was thoroughly mixed and homogenized to avoid any bias due to the sampling procedure. 20 sample cups containing about 30 g of the cement were inserted into the input magazine of the HR-LA 1. From here, the sample cups were transported alternately to HP-MP 2 or HP-MP 3 in such a way that each HP-MP processed ten samples.

We used identical preparation parameters both in HP-MP 2 and HP-MP 3, i.e., grinding time of 60 s at a rotation speed of 800 rpm. During the grinding process, three grinding aid tablets of the type HMPA 100 were added to each sample. Both HP-MPs were equipped with a sensor to record the average acceleration of each grinding trial. The acceleration signal was also used to determine the rotation speed of both HP-MPs using a Fast Fourier (FF) analysis. The analysis confirmed that both machines were operated at a rotation speed of exactly 800 rpm. Following the pulverizing process, the ground sample material was pelletized into a 51 mm steel ring. Again, identical pressing parameters were used in HP-MP 2 and HP-MP 3 (pressing force 100 kN, pressing time 30 s).

All pressed pellets were analyzed on the same XRF instrument (Bruker S4, Karlsruhe, Germany). The analytical data were collected by using the PrepMaster Analytics for further analysis. The mean average (mean wt%) and standard deviation (SD) of the element concentration were calculated after preparation of ten samples each in the HP-MP 2 or the HP-MP 3. We used the student's t-test (significance level of P value < 0.05) to determine whether there were statistically significant differences of XRF analytical results after sample preparation within HP-MP 2 vs. HP-MP 3.

Results

In the HP-MP 2 and HP-MP 3, sample preparation resulted in very precise XRF analyses. This was shown by the low standard deviation of the element concentrations after sample preparation in both machines (Figure 2, Table).

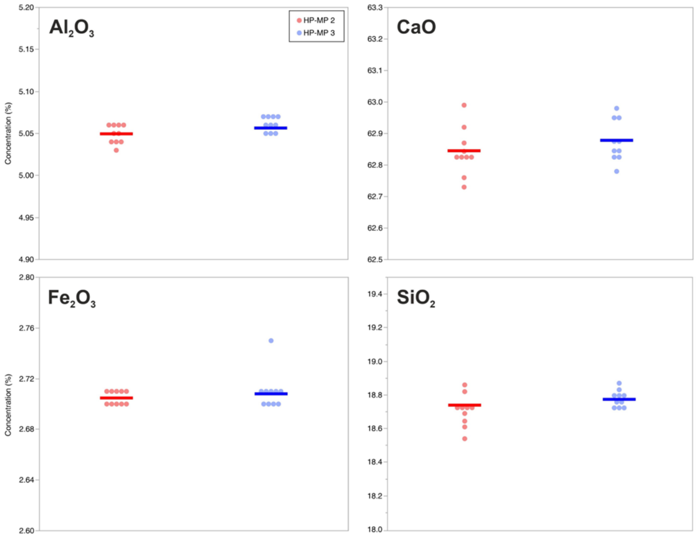

Figure 2: *Graphical display of XRF analysis of concentration of Al_2O_3, CaO, Fe_2O_3 and SiO_2 after sample preparation in the HP-MP 2 (red) and HP-MP 3 (blue).*

We compared the XRF results after preparation in HP-MP 2 to preparation in HP-MP 3. The differences of the mean element concentrations after preparation either in HP-MP 2 or HP-MP 3 were negligible (Table).

Accordingly, the student's t-test showed no significant differences (Table). Due to their low concentrations, the t-test could not be performed for K2O, Na2O and P2O5.

The mean acceleration (± SD) showed slightly higher values for grinding within the HP-MP 2 (25.04 ± 3.98 m/s2) compared to the HP-MP 3 (24.86 ± 3.67 m/s2) (Figure 3). The review of the time course of acceleration revealed a high repeatability of the grinding process within HP-MP 2 and HP-MP 3 (data not shown). The difference in acceleration was not statistically relevant as indicated by the student's t-test.

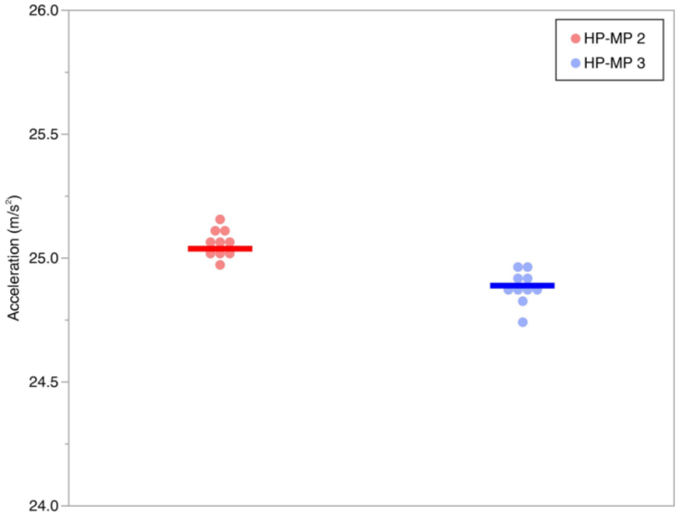

Figure 3: *Graphical display of the acceleration values obtained from the ten grinding cycles obtained within the HP-MP 2 (red) and the HP-MP 3 (blue).*

	Al_2O_3	CaO	Cl	Fe_2O_3	K_2O	MgO	Na_2O	P_2O_5	SO_3	SiO_2
Mean (wt%) HP-MP 2	5.06	62.88	0.02	2.71	0.33	1.22	0.09	0.32	2.82	18.78
SD (wt%) HP-MP 2	0.01	0.06	0.00	0.01	0.00	0.00	0.00	0.00	0.02	0.05
Mean (wt%) HP-MP 3	5.05	62.84	0.02	2.71	0.33	1.21	0.09	0.32	2.81	18.70
SD (wt%) HP-MP 3	0.01	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.09
Δ Mean (wt%) HPMP 2 vs. HP-MP 3	0.01	0.04	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.08
P value student's t-test	2.6983	1.0901	1.8973	1.0000	n.a.	4.2000	n.a.	n.a.	0.7869	2.1811

Table: *This table shows the analytical results as mean and standard deviation of the XRF element analysis after sample preparation within the HP-MP 2 (blue) and HP-MP 3 (grey). Furthermore, the differences between the two HP-MPs are displayed and the significance P values are calculated (yellow).*

Discussion

This study demonstrates that the HP-MP ensures a highly reproducible preparation of samples used for XRF analysis. The repeatability within each single machine was excellent as shown by the low standard deviation of XRF results for samples prepared either by the HP-MP 2 or HP-MP 3. Moreover, we could demonstrate that it did not matter whether the sample was prepared in HP-MP 2 or HP-MP 3. The differences in XRF results between the two HP-MPs were negligible and hence the outcome of the XRF results can be regarded as identical independent from the grinding/ pelletizing machine used for sample preparation. This provides the basic prerequisite for excellent repeatability within the laboratory, even when different sample preparation routes and combinations of machines are used.

Interestingly, the data shown here was not acquired under controlled experimental conditions but in the setting of an operating quality control cement laboratory. This illustrates that the high repeatability of the HP-MP is assured even under the demanding circumstances of a fully utilized cement laboratory. The HP-MPs have been in operation for several months and have already ground and pelletized thousands of samples. These data show that a low measurement uncertainty and small analytical error can also be achieved by using different disc mills in the daily laboratory routine.

The high degree of repeatability in analytical results is largely due to the high degree of repeatability of the grinding process. On the one hand, monitoring of the grinding process by means of the acceleration sensor showed low variability between the subsequent grinding cycles within each HP-MP. On the other hand, it could be demonstrated that the grinding processes are almost identical in both HP-MPs as revealed by comparison of the mean acceleration values obtained in HP-MP 2 and HP-MP 3. The difference in acceleration of 0.15 m/s^2 between HP-MP 2 and HP-MP 3 represents a deviation of less than 1 % and is therefore not significant in any way.

As part of the quality control process in the HERZOG factory, automatic disc mills including the HP-MP are tested for repeatability of the grinding process, grain size distribution and XRF analysis. Additionally, the real-time monitoring of the acceleration by the PrepMaster Analytics software allows the continuous assessment of the grinding performance in the laboratory environment and automatic detection of faults of the grinding set [3] and swing aggregate [4]. This study underlines the importance of reproducible sample preparation for testing laboratories to constantly ensure analytical validity.

References

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