Study on precision of dosing and XRF analysis in automatic sample preparation of clinker

Abstract

The HP-MP is an automatic laboratory mill/press combination applicable for sample preparation of cement products and other materials. Using the HP-MP, we investigated the influence of the input particle size of clinker and the vibration time of the integrated dosing spoon on the sample output weight and the results of XRF analysis. The input of fine clinker and a long vibration time resulted in significantly higher output weights than input of coarse clinker and a short vibration time or no vibration. For each clinker type and vibration time, the output weights were consistent with low variance. The XRF analysis showed that different output weights resulted in small but significant differences in compound concentrations. Again, the variance of XRF results was low. The findings demonstrate that 1. automatic sample preparation of the HP-MP results in high analytical precision and 2. material properties and sample preparation parameters influence the analytical outcome and should be considered during application development and monitoring.

Key words

• **Clinker** • **Dosing precision** • **XRF analysis** • **Grain size** • **HP-MP**

Introduction

The reliability of a chemical analysis by XRF depends strongly on accuracy and precision of sample preparation. A variety of factors can influence the preparation of sample material in a vibrating disk mill and the subsequent XRF analysis. Previously, we have demonstrated that the way in which the grinding vessel is manually loaded with sample material has a significant impact on the pulverizing efficiency [1]. Shaltout et al. [2] investigated the impact of the particle grain size for wavelength dispersive X-Ray fluorescence spectrometry and found a deviation of 10 %. Furthermore, Demir et al. [3] showed that the grain size effect reached up to 30 % share in total error.

In this application note, we investigate the influence of the input particle size of clinker samples and the execution of volumetric dosing on the sample output weight of a vibrating disc mill and the subsequent XRF analysis. For this study, we used Portland clinker as sample material which was further processed in the HP-MP mill/press combination.

Methods

Three subsamples were obtained from a batch of the same Portland clinker by representative splitting. Subsequently, each subsample was comminuted by means of the HSC 550 jaw crusher (Herzog, Germany) by adjusting different gap widths. This resulted in three subsamples categories with different particle size distributions: fine clinker (called “Fine”), coarse clinker (“Coarse”) and clinker with intermediate particle size distribution (“Medium”). Table 1 shows the D-values of the three different clinker subsamples.

Grain size category	D60 [mm]	D90 [mm]
Coarse	2.334	5.290
Medium	1.333	3.136
Fine	0.896	2.410

Table 1: *Distribution of grain sizes in the different subsample categories of clinker based on D values.*

The sample material was then fed into the HP-MP combined mill/press using a 100 ccm standard sample cup. In the HP-MP, volumetric dosing of the sample material was carried out by means of a hemispherical dosing spoon. Subsequently, the dosing spoon was vibrated for a definable time to compact the material. For this test, we used no vibration (0 s), 3 s, or 10 s of vibration. Afterwards, the excess material of the clinker cone was stripped off to achieve the defined hemisphere volume. Before the subsequent grinding process (120 s, 1400 rpm, 15 s discharge time) was started, four pills of the grinding aid type HMPA- 40 (Herzog, Germany) were automatically added to the grinding vessel.

In the first part of this study, we performed 30 trials for each clinker category (fine, medium coarse) in which 10 trials were carried out without vibration of the dosing spoon, 10 trials with 3 s of vibration, and 10 trials with 10 s of vibrations. This resulted in a total of 9 different conditions with a total of 90 trials (see Table 2). After completion of each grinding process, the entire sample material was discharged from the grinding vessel into a sample cup. The material amount of the discharged material was then weighed. We calculated the mean output weight and standard deviation (mean ± SD) for each condition and performed a student’s t-test to evaluate whether there are significant differences between the conditions.

Grain size category	Vibration time [s]	Condition
Coarse	0	C0
Medium	0	M0
Fine	0	F0
Coarse	3	C3
Medium	3	M3
Fine	3	F3
Coarse	10	C10
Medium	10	M10
Fine	10	F10

Table 2: *Classification of the samples according to grain size category and vibration time leading to nine different conditions. In each condition 10 trials were performed.*

In the second part of this study, we performed XRF analyses to investigate the impact of the grain size distribution and dosing mode on the analysis of the chemical composition. For this purpose, we performed 10 trials with coarse material being vibrated for 3 s (C3) and 10 trials with fine material vibrated for 10 s (F10). After completion of grinding, the material was pelletized in a 51.5 mm steel ring and analyzed. For XRF analysis, we used a S2 Puma EDXRF spectrometer (Bruker, Germany) with a single-point calibration as well as fixed current and voltage.

The primary focus of the XRF analysis was on the main components relevant for the control of clinker production. These include: CaO, SiO2, Al2O3 and Fe2O3. We also calculated the Lime Saturation Factor (LSF) from the oxides, which reflects the ratio of CaO to the other three oxides. The student’s t-test was used to determine statistical differences between main compound concentrations. The F-test was applied to investigate whether there are any differences in the variance of the mean compound concentrations.

Results

Influence of clinker grain size and vibration time of the dosing spoon on the sample output weight

Figure 1 shows the output weight of each of the three clinker categories (fine, coarse, medium) and the corresponding vibration duration of the dosing spoon (0 s, 3 s, 10 s). As a general observation, the mean output weight increased from coarse towards medium and fine grain size as well as with increasing vibration duration. We observed the lowest mean output weight (15.59 ± 0.58 g) for coarse clinker after dosing without vibration (C0). By contrast, the highest output weight (17.50 ± 0.18 g) was found for fine clinker after 10 s of vibration (F10).

Concurrently, the highest variability in the output weight was seen for the C0 condition (relative standard deviation RSD 3.7 %) whereas the F10 condition showed the lowest variability (RSD 1.0 %).

The student's t-test revealed three homogeneous groups (Figure 2): Group A included conditions F10, M10, F3 and M3 with output weight > 17 g, group B consisted of conditions C3, C10 and F0 leading to output weights between 16 and 17 g whereas group C contained conditions M0 and CO resulting in output weights below 16 g. Within each group, the t-test revealed no statistic difference between the output weights.

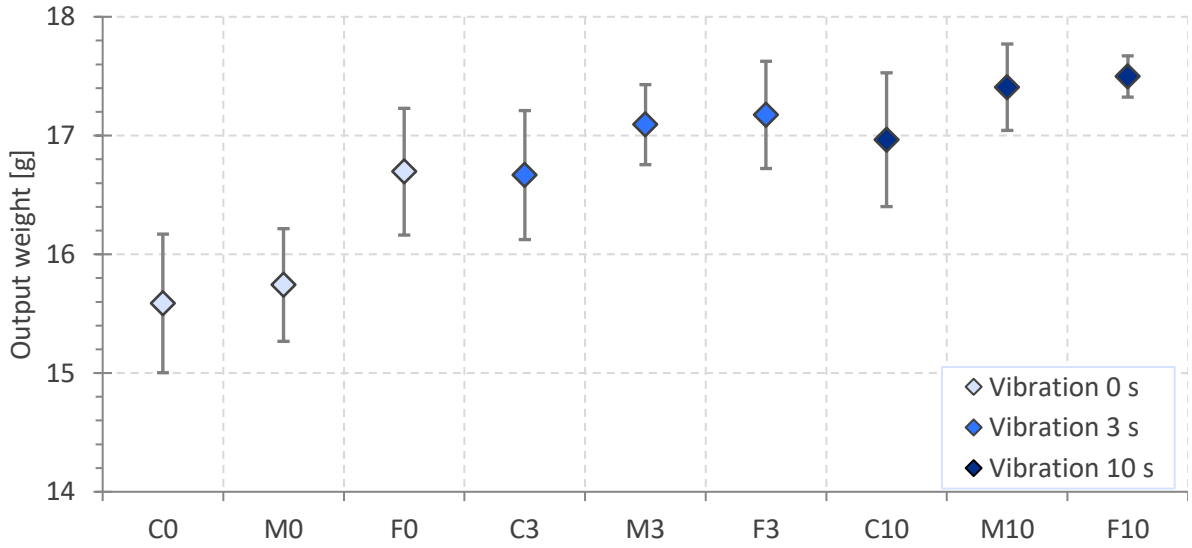

Figure 1: *Output weight of ground clinker for the nine different conditions. The conditions are sorted according to the applied vibration time of the dosing spoon from no vibration, 3 s vibration to 10 s vibration.*

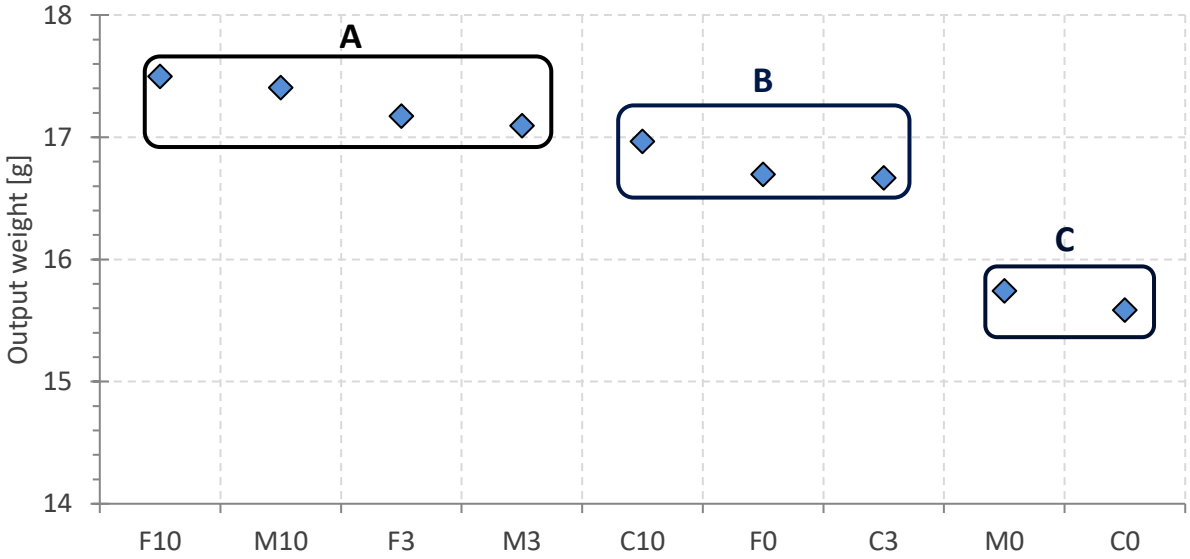

Figure 2: *Arrangement of conditions into homogeneous groups, which do not differ statistically in terms of output weight. Especially group C showed significantly lower output weights than the other conditions.*

Influence of clinker grain size and vibration time of the dosing spoon on the XRF analysis

Table 3 and Table 4 show the results of the XRF analysis from conditions C3 and F10. The tables show the main oxides as well as the resulting lime saturation factor (LSF) which is an important indicator in the production of cement. Here, we focused on the most important compounds for the cement production which are CaO, SiO2, Al2O3 and Fe2O3. Of those compounds, the highest relative standard deviation (RSD) in the C3 test series was Fe2O3 with 0.41 %. The highest RSD in the F10 test series was 0.38 % for Al2O3.

The F-test ($p > 0.05$) revealed no significant differences of the concentration variances between the conditions C3 and F10. In contrast, the t-test ($p<0.05$) showed significant differences in the element concentrations for CaO, SiO2, Al2O3 and Fe2O3. The maximum mean concentration difference was 0.33 % for CaO.

Sample ID	Al2O3 [%]	CaO [%]	Fe2O3 [%]	MgO [%]	Mn2O3 [%]	P2O5 [%]	K2O [%]	SiO2 [%]	Na2O [%]	SrO [%]	SO3 [%]	TiO2 [%]	LSF
1	4.79	65.69	3.09	0.969	0.076	0.221	0.723	21.76	0.067	0.049	0.604	0.255	95.77
2	4.76	65.79	3.08	0.963	0.076	0.220	0.721	21.74	0.066	0.049	0.612	0.253	96.05
3	4.78	65.81	3.11	0.965	0.077	0.221	0.704	21.76	0.067	0.049	0.594	0.255	95.94
4	4.80	65.73	3.11	0.968	0.077	0.220	0.710	21.68	0.066	0.049	0.600	0.254	96.13
5	4.82	65.63	3.12	0.969	0.076	0.221	0.722	21.73	0.066	0.049	0.591	0.254	95.74
6	4.77	65.64	3.10	0.963	0.076	0.220	0.703	21.63	0.066	0.049	0.597	0.253	96.21
7	4.78	65.74	3.09	0.974	0.076	0.221	0.718	21.81	0.066	0.049	0.608	0.254	95.68
8	4.80	65.72	3.11	0.969	0.076	0.220	0.717	21.79	0.067	0.049	0.607	0.255	95.69
9	4.77	65.79	3.09	0.963	0.076	0.220	0.698	21.75	0.066	0.049	0.583	0.252	96.00
10	4.79	65.65	3.11	0.962	0.076	0.221	0.719	21.71	0.067	0.049	0.597	0.255	95.91
Mean	**4.79**	**65.72**	**3.10**	**0.967**	**0.076**	**0.221**	**0.714**	**21.74**	**0.066**	**0.049**	**0.599**	**0.254**	**95.91**
SD	**0.02**	**0.06**	**0.01**	**0.004**	**0.000**	**0.001**	**0.009**	**0.05**	**0.000**	**0.000**	**0.008**	**0.001**	**0.18**
RSD	**0.31%**	**0.10%**	**0.41%**	**0.38%**	**0.52%**	**0.23%**	**1.20%**	**0.23%**	**0.74%**	**0.00%**	**1.39%**	**0.39%**	**0.19%**

Table 3: *Compound concentrations following XRF analysis of ten clinker samples of condition C3 (coarse clinker, 3 s vibration)*

Sample ID	Al2O3 [%]	CaO [%]	Fe2O3 [%]	MgO [%]	Mn2O3 [%]	P2O5 [%]	K2O [%]	SiO2 [%]	Na2O [%]	SrO [%]	SO3 [%]	TiO2 [%]	LSF
1	4.88	66.17	3.15	0.975	0.077	0.222	0.653	21.93	0.066	0.048	0.598	0.256	95.63
2	4.82	66.07	3.16	0.971	0.077	0.220	0.649	21.68	0.065	0.049	0.589	0.258	96.54
3	4.85	65.98	3.14	0.974	0.077	0.221	0.648	21.82	0.066	0.049	0.583	0.257	95.82
4	4.84	66.08	3.14	0.977	0.077	0.221	0.653	21.83	0.066	0.049	0.591	0.255	95.93
5	4.83	66.13	3.14	0.972	0.076	0.221	0.632	21.79	0.065	0.049	0.571	0.258	96.17
6	4.83	66.11	3.13	0.972	0.076	0.221	0.649	21.85	0.066	0.049	0.594	0.255	95.93
7	4.83	66.00	3.14	0.968	0.077	0.221	0.652	21.77	0.065	0.049	0.591	0.256	96.08
8	4.81	65.98	3.14	0.968	0.076	0.221	0.649	21.75	0.065	0.049	0.588	0.253	96.14
9	4.85	65.93	3.16	0.977	0.077	0.221	0.658	21.77	0.065	0.049	0.595	0.257	95.94
10	4.85	66.05	3.14	0.979	0.076	0.221	0.652	21.91	0.066	0.048	0.591	0.255	95.56
Mean	**4.84**	**66.05**	**3.14**	**0.973**	**0.077**	**0.221**	**0.650**	**21.81**	**0.066**	**0.049**	**0.589**	**0.256**	**95.97**
SD	**0.02**	**0.07**	**0.01**	**0.004**	**0.000**	**0.000**	**0.006**	**0.07**	**0.001**	**0.000**	**0.007**	**0.001**	**0.27**
RSD	**0.38%**	**0.11%**	**0.23%**	**0.37%**	**0.64%**	**0.20%**	**1.00%**	**0.32%**	**0.76%**	**0.82%**	**1.22%**	**0.58%**	**0.28%**

Table 4: *Compound concentrations following XRF analysis of ten clinker samples of condition F10 (fine clinker, 10 s vibration)*

Discussion

In this study we show that both input grain size distribution as well as vibration time of the volumetric dosing spoon have significant influence on the output sample weight and the outcome of XRF analysis.

The output sample weight was highest for fine and medium clinker which was vibrated for 3 and 10 s on the dosing spoon (Group A in Figure 2). It is reasonable to assume that the sample output weight corresponds to the sample amount metered out by the dosing spoon. The results of this study suggest that finer material most probably results in a higher bulk density on the dosing spoon and consequently in a higher sample output weight. The vibration of the dosing spoon additionally leads to compaction of the material within the spoon and further increases the output sample weight. This is consistent with the finding that medium and coarse clinker which was not vibrated (group C, Figure 2) had the lowest output weight.

The second part of this study showed that different sample output weights are associated with small yet significant differences in XRF

analysis results. The differences in the mean oxide concentrations are most probably due to a dilution effect of the sample by the grinding aid. The amount of the added grinding aid was identical in both conditions, i.e., four pills corresponding to 0.8 g. By contrast, the sample weight in the F10 condition (17.50 ± 0.18 g) was significantly higher than in the C3 condition (15.59 ± 0.58 g). Thus, the sample of the C3 condition was more diluted by the grinding aid leading to lower element concentrations in the C3 test series compared to the F10 test series.

Overall, the variance of the output weight as a measure of repeatability was low in all experiments. Nevertheless, there was a tendency towards even lower variances of the output weight for finer materials and longer vibration durations. Correspondingly, the relative standard deviation for fine material that was vibrated for 10 s (F10 condition) was 1.0 % while for coarse material that was not vibrated (C0 condition) it was 3.7 %. Interestingly, the small difference in the standard deviation of the output weight was not reflected by the XRF analysis. Accordingly, the F- test showed no significant differences in the variance of the XRF results. Overall, the relative standard deviations for all measured major compounds were low in both the C3 and the F10 condition. This indicates a high repeatability and precision of sample preparation and subsequent XRF analysis.

The results of this study exemplarily underline that sample preparation has a traceable and significant influence on analysis, e.g., by means of X-ray fluorescence spectroscopy. The findings show that both the properties of the input sample material and the adjustment of the parameters of the automatic sample preparation can influence the analytical outcome. During application development and monitoring, these influencing variables should be considered and controlled as effectively as possible.

References

[1] HERZOG Application note 27/2020: Impact of manual sample preparation on efficiency of grinding.

[2] Shaltout, A. A., Welz, B., & Ibrahim, M. A. (2011). Influence of the grain size on the quality of standardless WDXRF analysis of river Nile sediments. Microchemical journal, 99(2), 356-363.

[3] Demir, F., Şimşek, Ö., Budak, G., & Karabulut, A. (2008). Effect on particle size to emitted X-ray intensity in pellet cement sample analyzed with WDXRF spectrometer. Instrumentation Science and Technology, 36(4), 410-419.

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