Verification of suitability according to ASTM C114

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Preparation of cement samples using the POLAB® APM

Introduction

The ASTM standard C114 describes test methods for the chemical analysis of cement samples. The reference methods it describes are generally accepted classical analysis processes based mainly on wet-chemical methods. The standard also describes a procedure for verifying the suitability or qualification of alternative test procedures (performance requirements for rapid test methods).

X-ray fluorescence analysis (XRF) is a rapid, precise, long-established analysis technique for the quantitative determination of cement samples as well as raw materials and intermediates used in the cement manufacturing process. Alongside a qualified test technique, sample preparation is of vital importance in XRF analysis. Analysis samples are generally prepared in the form of fused tablets[1] or pressed tablets. Fused tablets have the advantage of eliminating mineralogical and grain size effects as well as significantly reducing matrix effects. However, the disadvantage is that their production is complex, time-consuming, costly and difficult to automate. As long as the samples to be analyzed come from the same cement plant and thus have a similar matrix and granulometric distribution, it makes sense to prepare the samples in the form of pressed tablets. Moreover, this is easy to automate and ideal when a large number of samples need to be prepared – for instance for product and process control in the cement manufacturing process.

The sample preparation module POLAB® APM is part of the laboratory automation system from thyssenkrupp Industrial Solutions and it is specially tailored to the preparation of samples, inter alia from the cement industry. The fully automated APM grinds the samples to a uniform granulometric distribution and presses them into a standardized steel ring to form tablets. The pressed tablets thus prepared are then ideal for x-ray fluorescence analysis as well as for x-ray diffractometry.

Below you will see how preparing cement samples using the POLAB® APM in combination with XRF analysis meets the requirements of the ASTM standard C114 and is thus qualified as an alternative test method for the chemical analysis of cement samples.

[1] by fusion, e.g. using lithium tetraborate

Tests and results

To verify the qualification of APM sample preparation in combination with XRF analysis as an alternative test method according to ASTM C114, in total seven certified reference samples[2] were prepared on a single day using a POLAB® APMplus. The reference samples were prepared gravimetrically in the APMplus using 12.0 g sample material and adding three POLAB grinding aid tablets. Adding a grinding aid

[2] Portland cements from the National Institute of Standards & Technology as well as from the Cement and Concrete Reference Laboratory

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ASTM C114 qualification in terms of precision

Element oxide	Concentration range [%]	Maximum difference between duplicates (day 1 - day 2) [%]	Limit value ASTM [%]	Compliance?
SiO_2	19.3 - 21.2	0,08	0.16	Yes
Al_2O_3	3.7 - 5.9	0.02	0.20	Yes
TiO_2	0.2 - 0.3	< 0.01	0.02	Yes
Fe_2O_3	2.1 - 4.5	0.01	0.10	Yes
Mn_2O_3	0.1 - 0.2	< 0.01	0.03	Yes
CaO	61.6 - 64.2	0.12	0.20	Yes
MgO	1.2 - 4.8	0.02	0.16	Yes
SO_3	2.2 - 4.4	0.04	0.10	Yes
P_2O_5	0.1 - 0.2	< 0.01	0.03	Yes
Na_2O	0.1 - 0.4	< 0.01	0.03	Yes
K_2O	0.4 - 1.2	0.01	0.03	Yes
Cl	0.00 - 0.02	0.001	0.003	Yes

Table 1

ASTM C114 qualification in terms of accuracy

Element oxide	Concentration range [%]	Difference between average of duplicates & certificate values [%]	Limit value ASTM [%]	Compliance?
SiO_2	19.3 - 21.2	0.2	0.2	Yes
Al_2O_3	3.7 - 5.9	0.1	0.2	Yes
TiO_2	0.2 - 0.3	0.01	0.03	Yes
Fe_2O_3	2.1 - 4.5	0.04	0.1	Yes
Mn_2O_3	0.1 - 0.2	< 0.01	0.03	Yes
CaO	61.6 - 64.2	0.2	0.3	Yes
MgO	1.2 - 4.8	0.1	0.2	Yes
SO_3	2.2 - 4.4	0.1	0.1	Yes
P_2O_5	0.1 - 0.2	< 0.01	0.03	Yes

Table 2

makes for more efficient particle size reduction as well as vacuum-resistant pressed tablets, and prevents the grinding bowl from becoming caked in the mill feed material. Each sample was ground for a period of 150 s at the lowest selectable speed.

Then, the pressed tablets were analyzed using an Axios Advanced XRF spectrometer from the company PANalytical. The spectrometer was calibrated using valid curve-fitting methods. The element oxides SiO_2, Al_2O_3, TiO_2, Fe_2O_3, Mn_2O_3, CaO, MgO, SO_3, P_2O_5, Na_2O and K_2O were measured as well as chlorine (Cl).

On a non-consecutive day, a new set of reference samples was prepared in the POLAB®APMplus and then analyzed. The difference between the analysis values obtained on day 1 and day 2 was determined for each of the element oxides measured, as was the mean value of the two measurements in each case. While the differences in the analysis values obtained on day 1 and day 2 are an indicator of the precision of the measuring method, comparing the mean values with the certified concentration values provides an indicator of the accuracy.

The results have been summarized in Table 1 (precision) and Table 2 (accuracy) along with the concentration ranges covered by the reference materials. The maximum variation determined for each element oxide in the seven reference materials is shown, and pursuant to ASTM C114 this must not exceed the respective limit value shown.

It can be seen from Table 1 that in the case of all element oxides the measured values are, with regard to precision, much lower than the limit values specified by the ASTM. With regard to accuracy (see Table 2), the measured values are also within the limit values specified by the standard.

Conclusion

X-ray fluorescence analysis is a long-established analysis technique, inter alia in the cement industry. The qualification of this method as an alternative test procedure in accordance with the ASTM standard C114 has already been verified in the past by manufacturers of such analytical instruments. Preparing cement samples as well as raw materials and intermediates used in the cement manufacturing process in the form of pressed tablets using the POLAB® APM has also a long proven success. Samples prepared in this manner are ideal for both x-ray fluorescence and x-ray diffraction analysis.

The present tests show that preparing cement samples using a POLAB® APM in combination with XRF analysis meets the performance requirements of ASTM C114 for alternative test procedures (performance requirements for rapid test methods). For all seven certified reference materials tested, the variations both in terms of precision (see Table 1) and in terms of accuracy (see Table 2) are lower or equal to the limit value specified in the standard. APM sample preparation in combination with XRF analysis thus qualifies as a rapid test method in accordance with ASTM.

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