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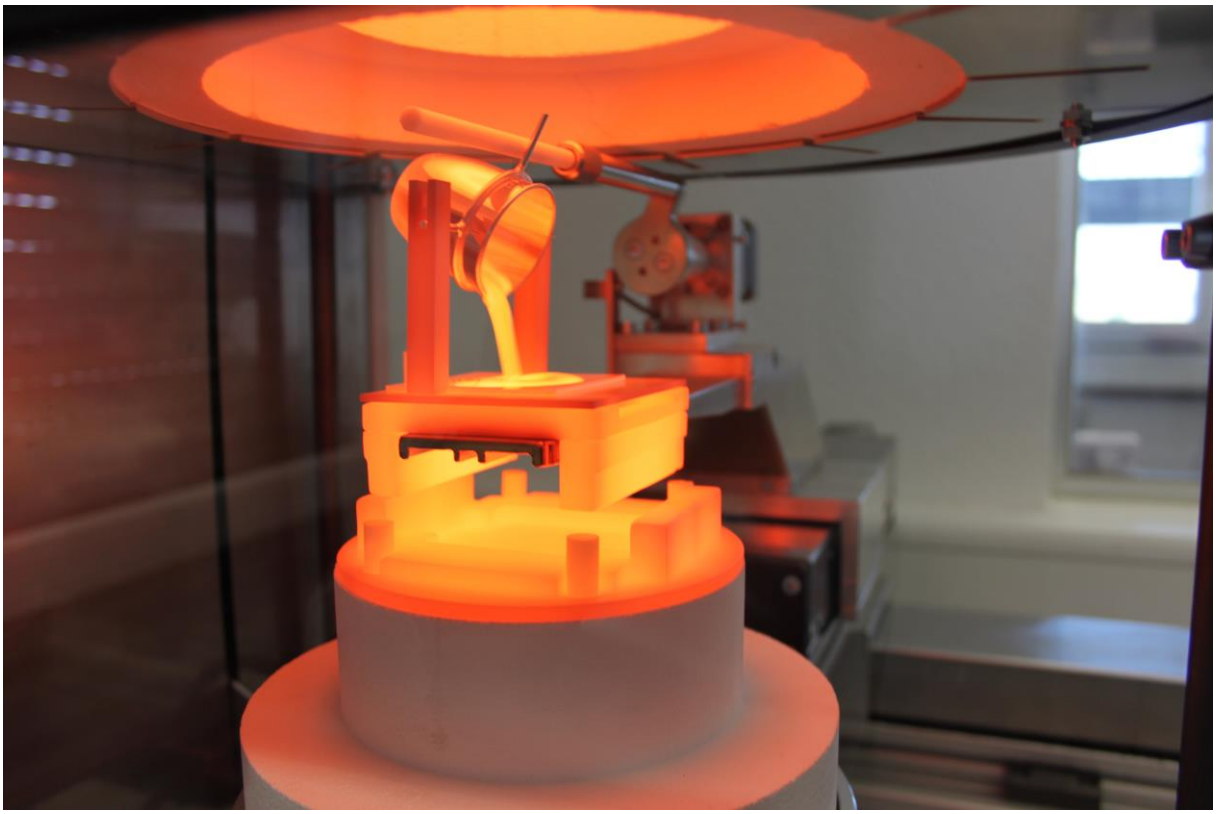
Fusion for X-Ray Fluorescence Analysis (XRF) with a New Automatic Electrical Fusion Furnace



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Introduction

In the cement industry, X-ray fluorescence analysis is used for quality control. Solid samples can be prepared as pressed pellets or fused borate beads. The pressed pellets are used whenever routine samples must be analyzed. One disadvantage to this method, however, is that the measurement signal for the pellet is dependent on matrix and grain size effects. When these must be excluded, then the sample must be prepared with fusion [1, 2, 3]. Here, the volatile elements, such as sulfur, chlorine or fluorine, become a problem. A new fusion furnace, developed within the framework of a ZIM project (sponsored by AiF, Berlin), makes it possible to reduce the volatility of these elements, thus improving the precision.

Fusion Technology

To make a fused bead, a mixture of the solid material and a glass forming material are heated so that a homogenous melt is produced. This is then poured into a mold and, after cooling, a glass bead with a defined surface, which serves as the measuring area for XRF, is formed. The goal of this form of preparation is to produce a reproducible, homogeneous distribution of the sample material in a glass

so that the original granulometry and structure of the substance no longer plays a role in measurement with XRF.

A fusion can be conducted with a muffle furnace, an induction oven or with a gas-fueled combustor. Predominantly platinum with 5% gold is used for the crucible material. The casting dishes are made from the same material.

If the fusion is manually conducted, the reproducibility of the quality of the generated glass depends on the talent of the person performing the fusion. Automatic fusion machines provide a better reproducibility.

Loss of Certain Elements During the Fusion

The volatility of some elements, like the halogens fluorine and chlorine or also sulfur, is more strongly influenced by the ambient conditions during the fusion process than other elements. For this reason, some of the currently available automatic fusion machines do not always provide satisfying results.

Reducing the Loss

The new fusion procedure presented here reduces the volatility with three technical innovations:

1. Only one sample is melted with reproducible conditions in a small closed muffle furnace.
2. In order to minimize heat loss when opening, the furnace door on the floor of the furnace is opened downwards with a lift, i.e., it is a so-called lift-bottom furnace.
3. The crucible is closed with an additional cover, so that only few losses are possible during the entire fusion.

Further important improvements increase the precision:

4. Filling of the oven with crucibles and casting dishes is automatically performed by an autosampler, so that positioning of the samples is reproducible.
5. Mixing of the sample with the flux is conducted by external rotation of the oven bottom in both directions (clockwise and counter clockwise).
6. The autosampler pours the melt into the casting dishes when it removes the crucibles.

Application of the New Fusion Furnace with a Cement Sample

Typical applications for fusion can be found in the cement industry. The new fusion technology presented here was tested for the quality control of cements in accordance with ISO 29581-2:2010 [4], to demonstrate the categorical efficiency and functionality of the new fusion furnace.

For the preparation, 1 g cement sample, which was to dried at 950 °C to constant mass, was mixed with 8 g 66% Lithium tetraborate + 34% Lithium metaborate (FX-X65 from the company FLUXANA) and placed into a platinum crucible (95% Pt+5% Au). The fusion was conducted for 10 minutes at 1200 °C. The melt was then poured into a 40 mm casting dish (95% Pt+5% Au).

Table 1 shows the results for 12 preparations of the same cement measured with a wavelength dispersive X-ray fluorescence instrument (PerformX from Thermo) within 14 days. According to ISO

29581-2:2010, the standard deviation of the repeatability for the “expert” performance must be smaller than a third of the limits given in the standard. Table 2 shows the results from 6 preparations of the NIST 1888b standard. According to ISO 29581-2:2010, the standard deviation in the accuracy for the “expert” performance must be smaller than the limits given in the standard. Both conditions were more than satisfactorily fulfilled with the method presented here.

Table 1: Preparations of the cement (FLX-CRM 100) within 2 weeks to test the repeatability.

FLX-CRM 100	Al2O3	CaO	Fe2O3	K2O	MgO	Na2O	P2O5	SiO2	SO3
Prep #1	5,56	64,49	2,61	0,84	1,47	0,24	0,16	20,80	2,95
Prep #2	5,57	64,50	2,63	0,85	1,46	0,24	0,16	20,84	2,93
Prep #3	5,55	64,42	2,62	0,83	1,48	0,24	0,16	20,82	2,97
Prep #4	5,56	64,45	2,62	0,84	1,47	0,24	0,16	20,84	2,95
Prep #5	5,55	64,51	2,61	0,85	1,49	0,24	0,16	20,82	2,95
Prep #6	5,54	64,49	2,62	0,85	1,47	0,24	0,17	20,77	2,94
Prep #7	5,56	64,37	2,63	0,85	1,48	0,25	0,16	20,79	2,96
Prep #8	5,55	64,40	2,61	0,84	1,48	0,24	0,16	20,80	2,94
Prep #9	5,57	64,49	2,60	0,84	1,48	0,23	0,16	20,81	2,91
Prep #10	5,56	64,43	2,61	0,84	1,49	0,23	0,16	20,79	2,93
Prep #11	5,57	64,31	2,60	0,85	1,47	0,23	0,16	20,78	2,96
Prep #12	5,56	64,37	2,60	0,85	1,47	0,23	0,16	20,77	2,95
Average	**5,56**	**64,44**	**2,61**	**0,84**	**1,48**	**0,24**	**0,16**	**20,80**	**2,95**
Stand. Dev.	0,010	0,063	0,009	0,005	0,008	0,006	0,001	0,024	0,016
Repeatablility limit	**0,07**	**0,23**	**0,05**	**0,03**	**0,04**	**0,02**	**0,02**	**0,13**	**0,05**

*according to ISO 29581-2:2010 for “expert performance”

Table 2: Preparations and measurement results for the cement sample (NIST 1888b) to test the accuracy.

NIST 1888b	Al2O3	CaO	Fe2O3	K2O	MgO	Na2O	P2O5	SiO2	SO3
Certificate	**4,37**	**64,44**	**3,13**	**0,67**	**3,64**	**0,14**	**0,07**	**20,85**	**2,69**
Accuracy limit*	0,08	0,25	0,08	0,03	0,08	0,02	0,02	0,15	0,08
Prep #1	4,38	64,49	3,13	0,65	3,61	0,15	0,07	20,81	2,64
Prep #2	4,36	64,43	3,12	0,64	3,61	0,14	0,07	20,77	2,65
Prep #3	4,38	64,49	3,12	0,64	3,63	0,14	0,07	20,81	2,66
Präp #4	4,36	64,41	3,12	0,65	3,61	0,16	0,07	20,83	2,66
Prep #5	4,36	64,37	3,11	0,65	3,61	0,14	0,07	20,79	2,66
Prep #6	4,37	64,48	3,12	0,65	3,62	0,15	0,07	20,82	2,66
Average	**4,37**	**64,45**	**3,12**	**0,65**	**3,61**	**0,14**	**0,07**	**20,81**	**2,65**
Stand. Dev.	0,008	0,049	0,007	0,002	0,008	0,008	0,001	0,023	0,009
Bias	**0,00**	**0,01**	**-0,01**	**-0,02**	**-0,03**	**0,01**	**0,00**	**-0,04**	**-0,04**

*according to ISO 29581-2:2010 for “expert performance”

Using the example of fusion of cement samples, it could be clearly demonstrated that all of the elements could be precisely determined. This was especially true for sulfur and the sometimes volatile alkalis, such as sodium or potassium.

Application of the New Fusion Furnace with Halogenated Compounds

The situation is different for samples that contain halogens. Examinations during the project have shown that during the fusion of a sample with a gas-fueled combustor, the chlorine recovery can fall between only 50-60% and only 60% for the fluorine recovery.

Through use of the newly developed closed fusion furnace and covering of the crucible during the entire fusion, the volatility could be significantly reduced and the recovery of chlorine and fluorine increased to up to 80% (Fig. 1).

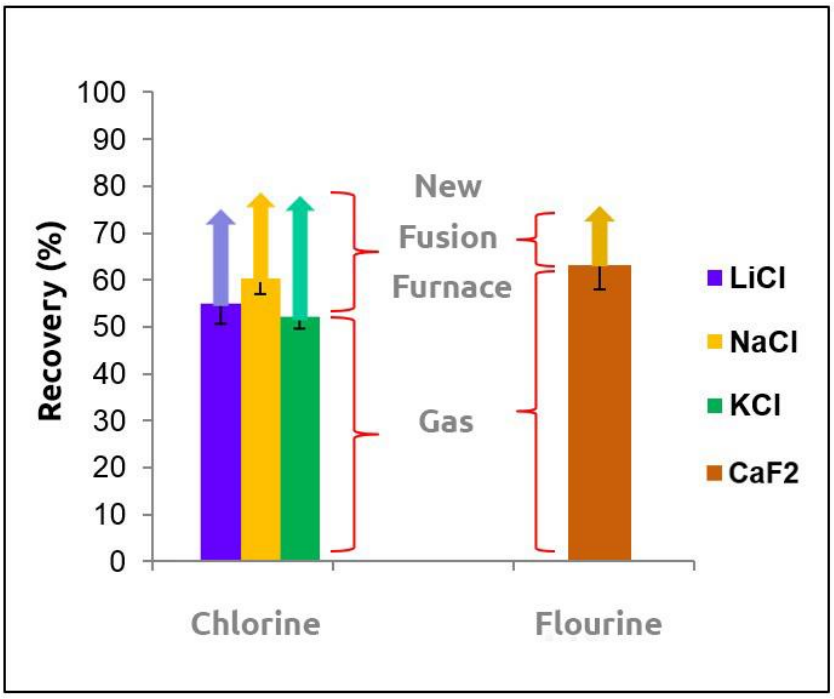

Fig. 1: With the new fusion method, the volatility of chlorine and fluorine could be reduced and the recovery increased to up to 80%.

Application Chlorine in Hot Meal and Bypass Dust

According to EN 196-2:2013 [5], as a reference method, chlorine is determined wet chemically via titration.

For the preparation, 1 g non-dried sample (hot meal or bypass dust from the cement industry) is mixed with 8 g FX-X65 and placed into a platinum crucible. The fusion was conducted for 10 minutes at 1200 °C with a cover. Afterwards, the oven was poured into a casting dish.

As a result, Figure 2 shows the calibration of chlorine in hot meal conducted with wavelength dispersive X-ray fluorescence analysis (WDXRF). The standard deviation (RMS) achieved was 0.02%.

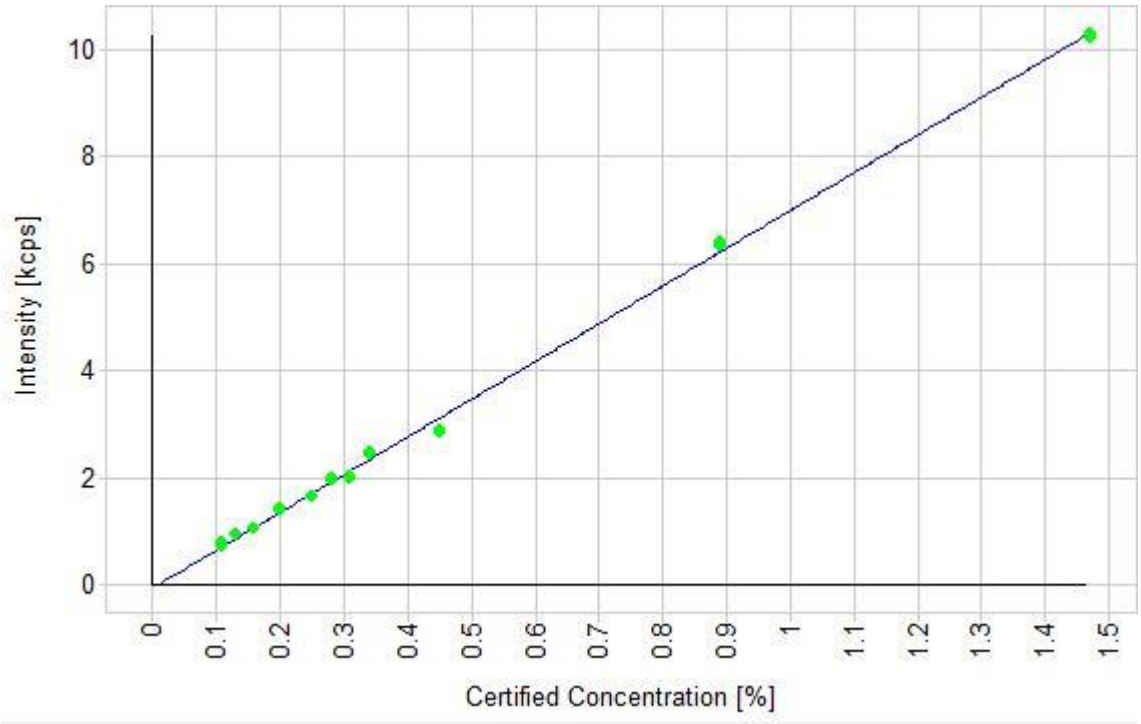

Fig. 2: WDXRF calibration curve for chlorine in hot meal measured as fused beads with a standard deviation RMS=0.02%; reference values from the titration.

As a result, Figure 3 shows the calibration of chlorine in bypass dust, provided by Dyckerhof Wiesbaden, conducted with wavelength dispersive X-ray fluorescence analysis (WDXRF). The standard deviation (RMS) achieved was 11%.

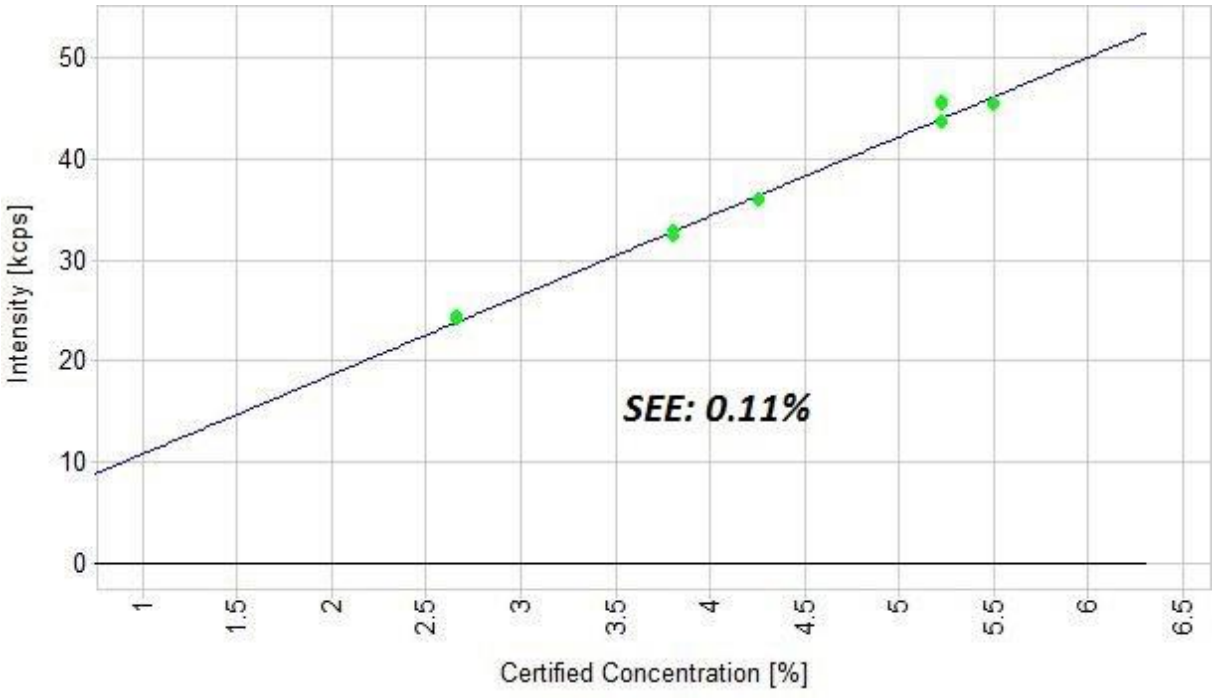

Fig. 3: WDXRF calibration curve for chlorine in bypass dust measured as fusion beads with a standard deviation RMS=0.11%; reference values from Wilhelm Dyckerhoff Institute determined via titration.

Summary

The fusion furnace developed within the framework of the ZIM project produces fused beads with a precision that corresponds to “expert performance” according to the ISO 29581-2:2010 cement standard. This result is based on the interaction between the lift-bottom furnace with a reproducible temperature profile and simultaneous use of covers on the crucibles. For volatile elements such as chlorine, fluorine or sulfur, the volatility can be significantly reduced compared to conventional fusion machines based on muffle ovens, induction ovens or gas-fueled combustors. Thus, the development of new application areas are made possible for XRF in combination with the fusion method of sample preparation.

[1] R.Schramm (2012): **Röntgenfluoreszenzanalyse in der Praxis.** FLUXANA, Bedburg-Hau.

[2] Hahn-Weinheimer, P., Hirner, A., Weber-Diefenbach, K. (1995): **Röntgenfluoreszenzanalytische Methoden: Grundlagen und praktische Anwendungen in den Geo-, Material- und Umweltwissenschaften.** Vieweg, Braunschweig/Wiesbaden.

[3] James P. Willis, Andrew R. Duncan (2008): **Understanding XRF Spectrometry Volume 1 Basic concepts and instrumentation, Volume 2 Quantitative analysis and special sample preparation and presentation methods.** Panalytical, Almelo, Netherlands.

[4] ISO 29581-2:2010 **Cement — Test methods —Part 2: Chemical analysis by X-ray fluorescence**

[5] DIN EN 196-2:2013 **Prüfverfahren für Zement – Teil 2: Chemische Analyse von Zement**