



Lab Report XRF 102

S8 TIGER[™]

The Determination of Sulfur Species (Sulfide – Sulfate) in Cement by WDXRF

Introduction

The examination of the sulfate concentration in cement is vital, because the presence of high amounts of sulfate delays the hydration of the aluminate phase. Especially for blast furnace slag cement the total concentration of sulfur and the ratio of the two sulfur species finally determines the cement quality. Traditionally the sulfate concentration is analyzed with wet chemical methods requiring long analysis time combined with high costs.

In general, X-ray fluorescence (XRF) is used to determine the total concentration of the elements. However, today the analysis of the different chemical compounds of lighter elements such as sulfur is possible by using wavelength dispersive XRF (WDXRF) with modern high resolution analyzer crystals. The different chemical compositions of the sulfur species will cause a peak shift, which can be used to separate both sulfur compounds, sulfate (SO_4^{2-}) and sulfide (S^{2-}) and determine the concentrations. The results can be used to calculate the slag concentration by subtracting the part derived from cement from the total sulfur concentration. This report explains how the modern sequential WDXRF spectrometer S8 TIGER performs speciation of sulfur in cement samples.



Picture. 1: S8 TIGER WDXRF spectrometer

Chemical speciation with XRF

The outer electrons of lighter elements up to the atomic number 18 are present in the atomic shells which are important for the emission of X-ray fluorescence lines. Sulfur has 6 valence electrons in the M-Shell. Any change in the oxidation state and therefore in the number of electrons in this shell will affect the K_{β} line of sulfur.

In cement there are two sulfur species present: Sulfide (S^{2-}) and sulfate (SO_4^{2-} , calculated as SO_3 in cement). Sulfide has 8 electrons in total, in the M-shell, while sulfate has no electron left in the important outer shell. This difference leads to changes in the spectrum, which can be used for the specification of the sulfur compounds:

- The X-ray line shifts (chemical shift)
Both the K_{α} and K_{β} lines show a shift of the line position. The physical reason is a shift of the energy levels caused by the chemical bonding influence.
- Additional X-ray lines appear (Satellite lines)
There is a significant difference concerning the presence of an additional line on the low energy side of the K_{β} line of sulfate, but not for sulfide.
- Changes in the ratio between K_{α} and K_{β}
The sulfide/sulfate ratio can be calculated based in the K_{α}/K_{β} ratio with respect to the total sulfur concentration.

Quantitative Determination

For the quantification of sulfide and sulfate the samples are analyzed with the sequential WDXRF spectrometer S8 TIGER. The S K_{β} line is measured by using the fine collimator with an opening of 0.23° and the high resolution crystal XS-Ge-C. This curved crystal provides a higher resolution and increased sensitivity for sulfur in comparison to traditional crystals, leading to a better analytical performance. The absolute precision of the goniometer positioning is vital for the accurate determination of the sulfur species. The S8 TIGER owns a high precision mechanical goniometer with ElectronicGearing for the optimized simultaneous rapid and reproducible positioning of all system components. This ensures the optimum resolution of neighboring peaks. The spectra of two samples with pure sulfide (red) and sulfate (grey) are shown in figure 1. In figure 2 spectra of real blast furnace slag cements are shown.

In both spectra the effects of the chemical bonding on the spectrum can be seen. The S K_{β} line shows a clear peak shift of about 0.2° (2θ). This difference is typically too small for a routine determination of the two compounds. The intensity of the S K_{β} line is composed by the emission of sulfide and sulfate. But sulfate in addition has a satellite line on the low energy side, the so called S K_{β} SX line. The difference of the peak positions is about 0.68° (2θ), which can be clearly resolved. The total sulfide concentration can now be analyzed using the K_{β} line. The part from sulfate is subtracted by defining a line overlay correction based on the satellite line S K_{β} SX.

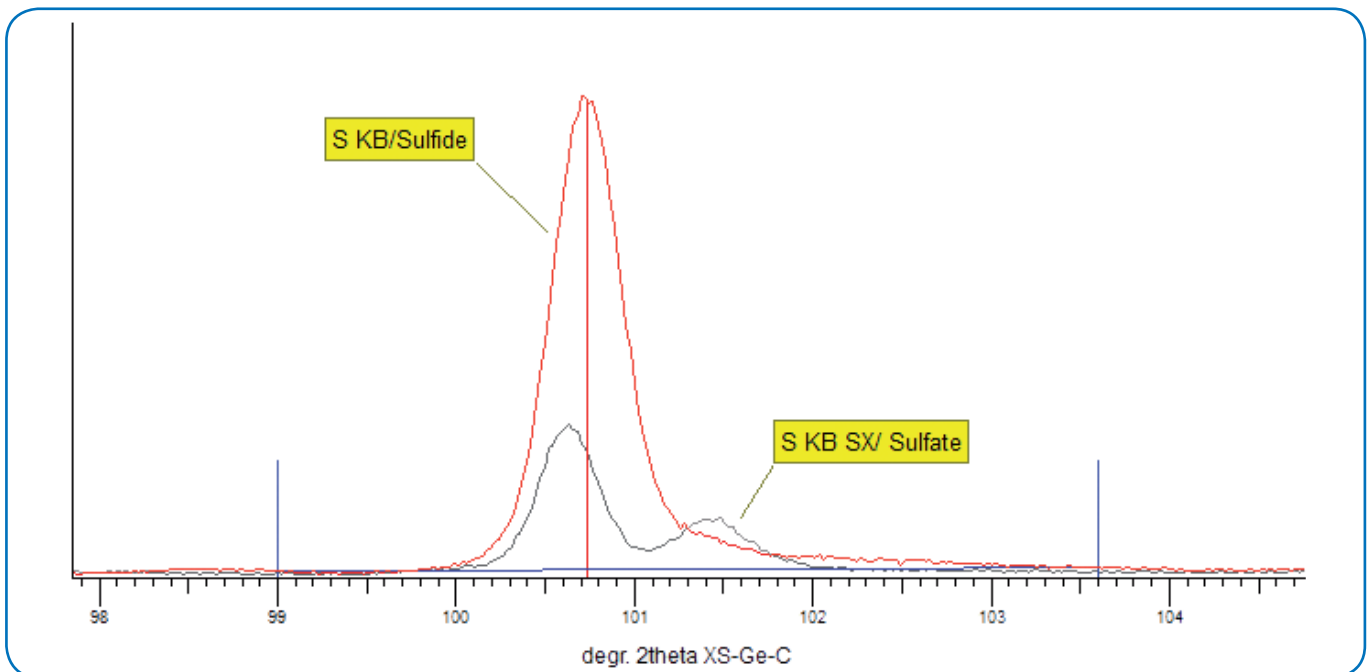


Fig. 1: Set of sample spectra - pure sulfide sample is highlighted in red, the spectral background is colored blue, and sulfate is shown in grey

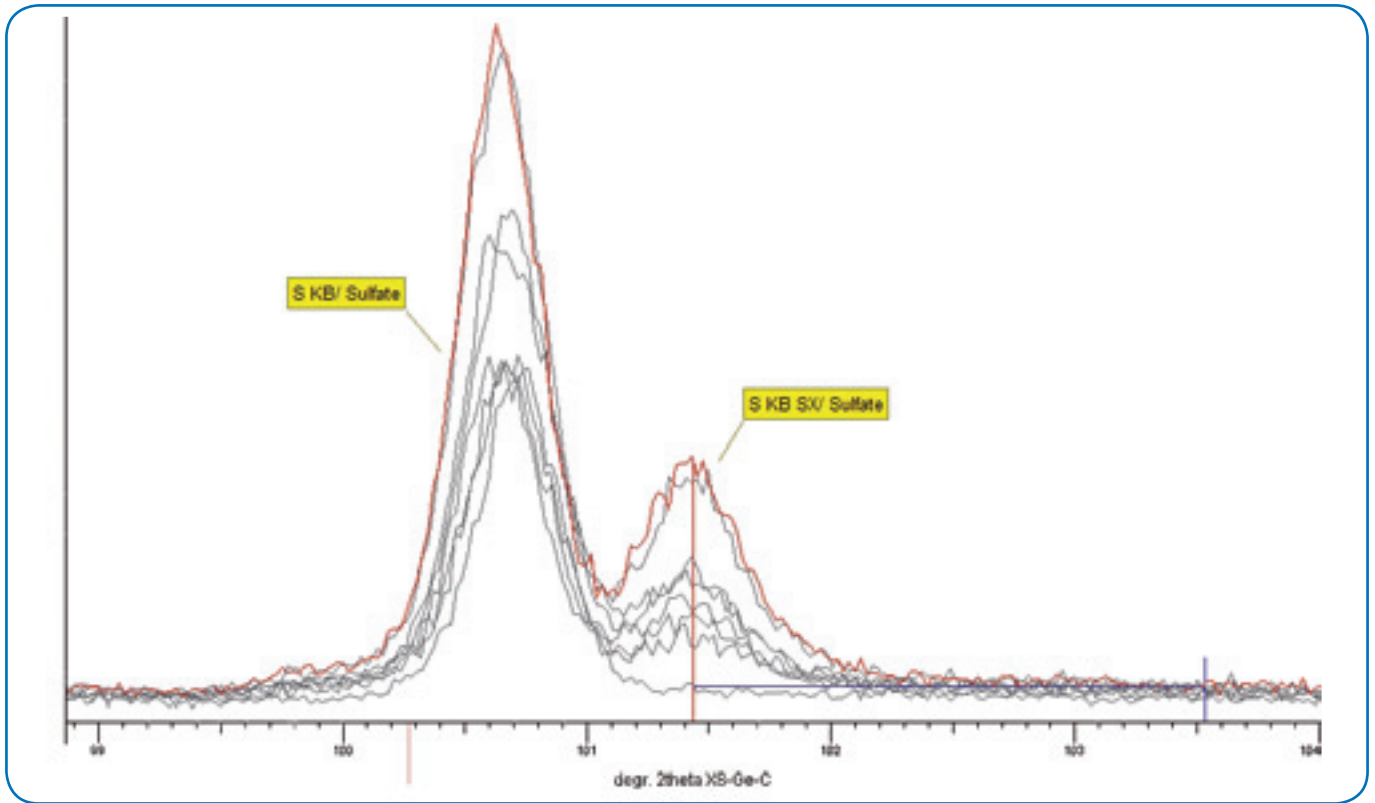


Fig. 2: Set of blast furnace slag cements with varying concentrations of sulfide and sulfate.

Calibration

The S8 TIGER was calibrated using a set of 8 cement samples with varying concentrations of sulfide and sulfate. In addition also the ratio between both compounds was not constant. The samples were freshly prepared as pressed powder. For this 10 g sample was milled with 3 tabs of cellulose grinding aid

and then pressed with 20 tons for 20 seconds in aluminum cups. Measurement time was 60 seconds for each line and 30 seconds for two common backgrounds. The calibration curves for both sulfur species are shown in fig. 3 and fig.4. Results of calibration standards are shown in table 1.

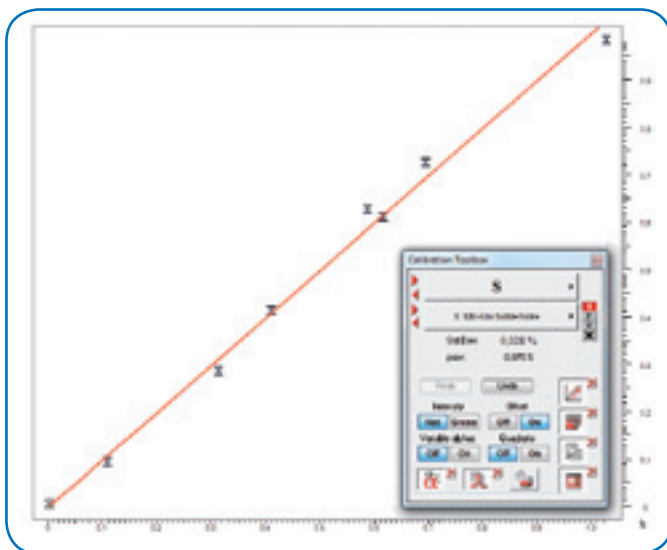


Fig. 3: Calibration Curve for sulfide by applying line overlap correction

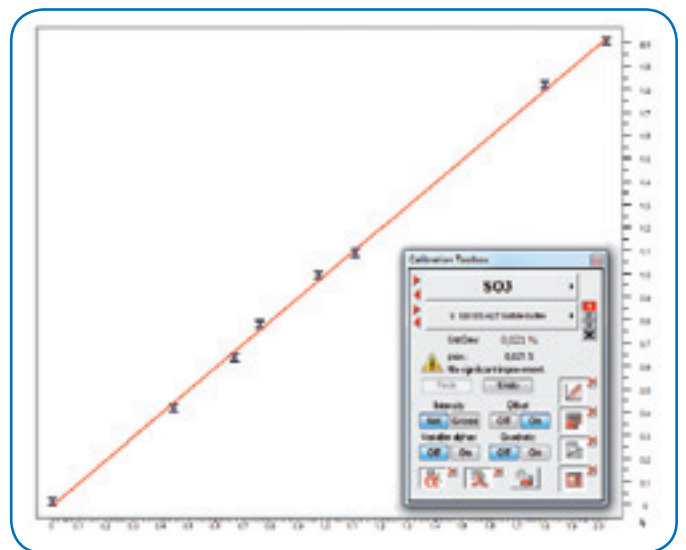


Fig. 4: Calibration Curve for sulfate

Table 1: The results for some calibration standards

Sample name	Reference S ²⁻ [%]	Measured S ²⁻ [%]	Abs. Diff.[%]	Reference SO ₃ [%]	Measured SO ₃ [%]	Abs. Diff.[%]
S1	0	0.0059	0.0059	1.1068	1.0909	0.0159
S2	1.0254	0.9838	0.0416	0	0.0155	0.0155
S3	0.1074	0.0945	0.0129	2.022	2.0061	0.0159
S4	0.6934	0.7258	0.0324	0.7587	0.7808	0.0221
S5	0.4102	0.4135	0.0033	0.6649	0.6394	0.0255
S6	0.5859	0.6283	0.0424	0.9739	0.9955	0.0216
S7	0.3125	0.286	0.0265	1.7991	1.8187	0.0196
S8	0.6152	0.6122	0.003	0.442	0.4206	0.0214

Stability and repeatability

One additional cement sample was measured 10 times to check the stability and repeatability of the method. Table 2 shows the results of stability measurement.

Table 2: Results of the stability test

	S ² [%]	SO ₃ [%]
reference	0.758	2.093
1	0.759	1.995
2	0.762	1.998
3	0.760	1.991
4	0.766	2.062
5	0.754	2.029
6	0.759	2.015
7	0.740	2.021
8	0.768	1.995
9	0.767	2.034
10	0.762	2.039
average	0.756	2.018
std. dev.	0.008	0.023

Results and Conclusions

The analysis of sulfide and sulfate in cement samples for quality control can be realized on a daily routine based on WDXRF. The S8 TIGER with the high resolution setup, applying the fine collimator and the curved crystal XS-Ge-C allows the accurate and reproducible analysis of neighboring peaks. The differences between the reference values and the measured concentrations are in the very low ppm range while the total concentrations of sulfur in the cement are in the range of 3 to 5 %. This report demonstrates that WDXRF can completely replace time consuming wet chemical procedures in the cement laboratory.

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