Calibration of Sulfate and Sulfide in Cement with the Set of Fluxana Standards FLX-CRM 113-122

Introduction

Especially for blast furnace cement, the total sulfur concentration and the proportion of sulfate to sulfide is decisive for the quality of the cement. Sulfate is one of the important components of the cement that ensures that the cement bonds. If blast furnace slag is mixed with the cement (the case for blast furnace cement), then only sulfide sulfur from the blast furnace slag of the granulated slag, which plays no role during binding of the cement, is added as a component. The sulfide sulfur is not distinguished from sulfate sulfur during normal analytical methods, such as combustion or those based on fusion. The sulfate proportion is traditionally determined using a wet chemical procedure, which is time consuming and expensive.

Generally, an XRF instrument is used to determine the concentrations of the elements in a sample. Today it is, in addition to being able to determine the lighter elements, also possible to distinguish between the different chemical sulfur compounds using high resolution crystals. The different chemical environments from sulfate and sulfide cause a peak shift that can be utilized to determine the concentrations of both. With the results, it is possible to calculate the concentration of the blast furnace slag by subtracting the derived portion from the total sulfur in the cement.

Quantitative Determination

In order to quantify sulfate and sulfide, a WDXRF instrument is used to measure the S $K_{\beta 1}$-line, because it shows a clear peak shift. A high resolution germanium crystal combined with the narrowest possible collimator, e.g., 0.15°, enables quantification of sulfate in addition to quantification of the total sulfur with a wider collimator of 1.00°. The S $K_{\beta 1}$-line is measured for quantification of the total sulfur and the S $K_{\beta 1}$ satellite-line for quantification of the sulfate. The two lines are about 0.68° (2θ) apart (see Figure 1 and Figure 2). The sulfide portion can be quantified by subtracting the sulfate portion from the total sulfur content. Thus, using the S $K_{\beta 1}$-line, the sulfide content of the sample can be indirectly quantified.

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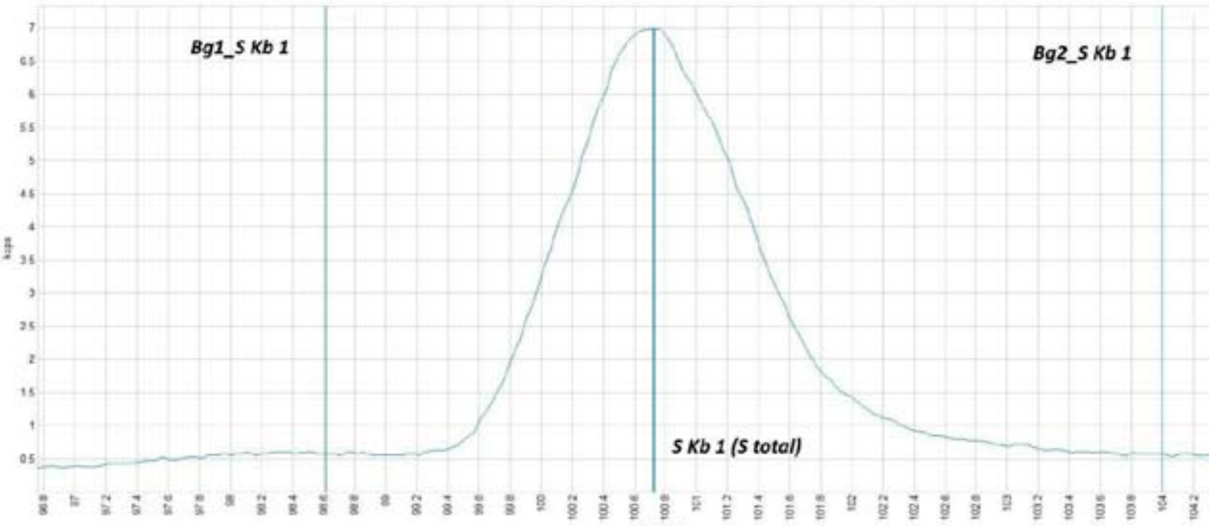

Figure 1: Scan of the sample with the highest sulfide content (FLX-CRM 116); the S $K_{\beta1}$-line, used to determine the total sulfur content, can be seen (measuring conditions: germanium crystal, FPC detector, collimator 1.00°, 30 kV, 80 mA)

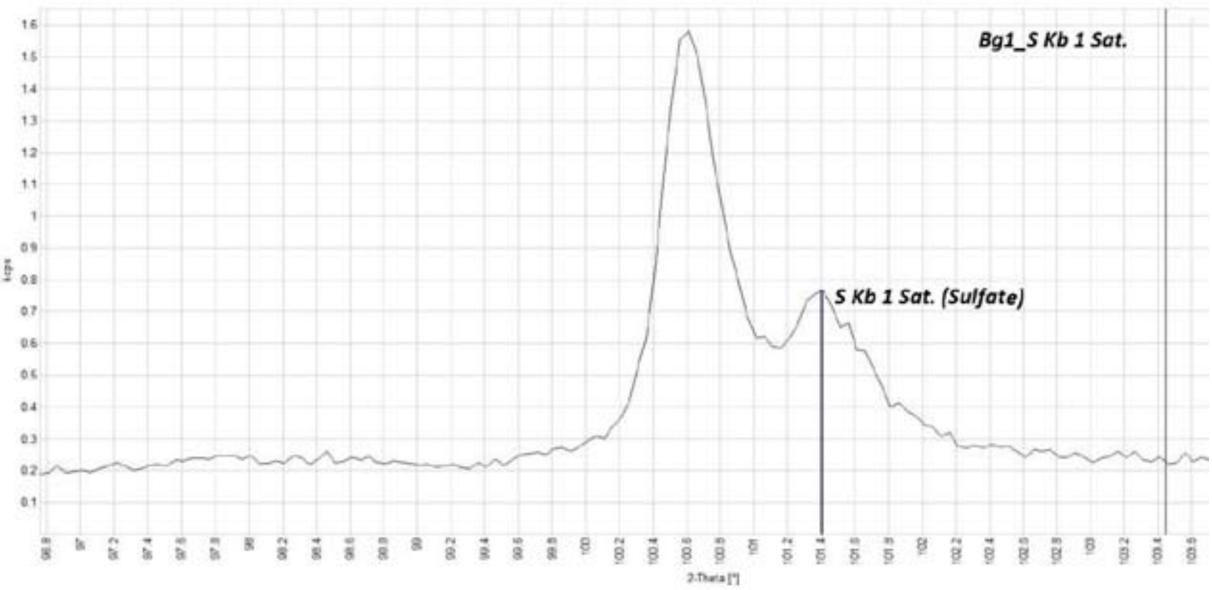

Figure 2: Scan of the sample with the highest sulfate content (FLX-CRM 119); the S $K_{\beta1}$ satellite-line, used to determine the sulfate content, can be seen (measuring conditions: germanium crystal, FPC detector, collimator 0.15°, 30 kV, 80 mA)

Calibration

The method is calibrated with 10 certified cement samples with varying sulfate and sulfide concentrations (only sulfate concentrations are certified, sulfide is reported as information value only). The FLX-CRM 113-122 set is a suitable calibration set. The cement is finely ground and mixed with Cereox with a ratio of 4:1 (e.g., 4 g cement + 1 g Cereox for a pressed pellet with a 32 cm diameter) and pressed with 20 t. The measuring time for the S K_{β}-line is 10 s; the corresponding background lines also 10 s each; and the S $K_{\beta 1}$-satellite-line and corresponding background line 60 s each.

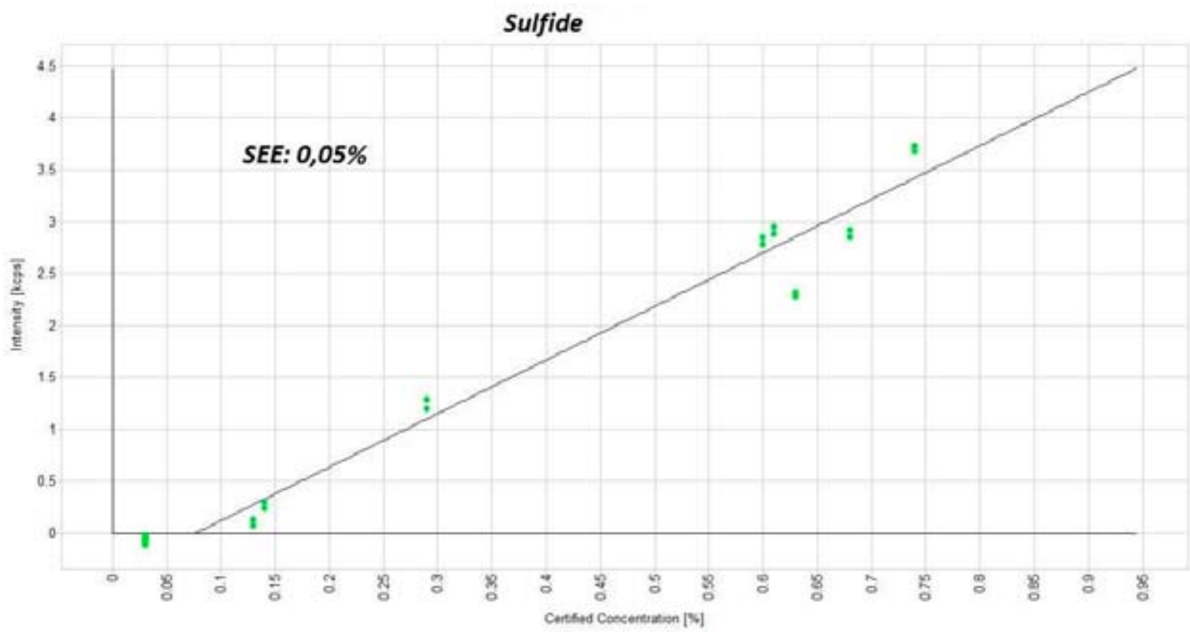

Figure 3: Calibration line for the sulfide quantification, enabled by calculation of the difference between the intensities determined for the total sulfur content and the sulfate content.

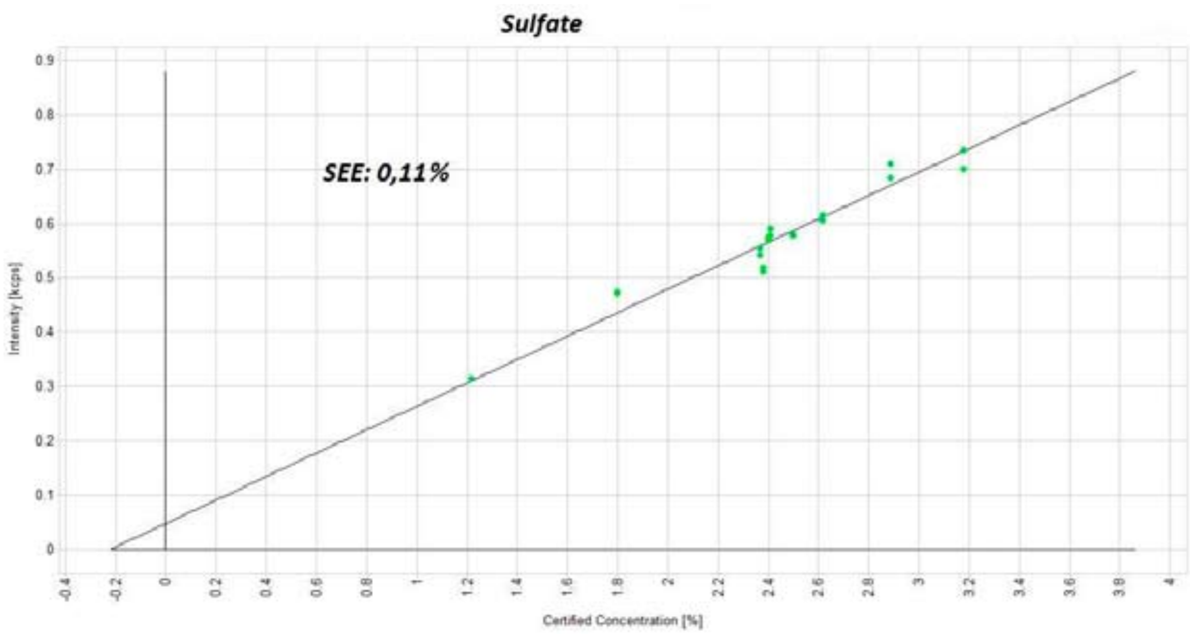

Figure 4: Calibration line for the sulfate quantification

Validation

To validate the method, cements from different origins were measured and tested for the sulfate content.

Table 1: Results for various cements from different origins

Sample	Reference SO_4^{2-} as SO_3 %	Measured SO_4^{2-} as SO_3 %
1	3.67	3.64
2	2.49	2.43
3	2.76	2.74
4	2.86	2.76
5	3.53	3.55

Summary

The analysis of sulfate and sulfide in cement can become daily routine using a WDXRF instrument; replacing time consuming wet chemical analysis. Preparation and measurement of pressed pellets is inexpensive and requires little time. The validation confirms that the method developed by FLUXANA with the now commercially available cement set (FLX-CRM 113-122) can be used for cement from different origins.