



Lab Report XRF 94

S8 LION⁽⁽⁽

Rapid Free-Lime Quantification in Clinker for Cement Process Control

Introduction

Today one of the main aims of successful cement production is low energy consumption combined with a high product quality. An important process parameter is the free-lime concentration in the clinker produced in the kiln process. When this concentration is maintained at a level typically between 1 and 1.5% – the actual value is largely dependent on local conditions – optimum energy consumption with maximum reactivity of the kiln is achieved. Thus close monitoring of the free-lime concentration in the clinker enables the optimum operating conditions to be exactly determined. When the kiln is run under these conditions, considerable fuel savings and thus a reduction of CO₂ emissions can be achieved.

Furthermore, determination of the free-lime content benefits cement quality. An excess of free lime in cement can result in expansion effects.

Traditionally, free-lime content is measured using wet chemical methods such as titration, which lasts 35-45 minutes and has a relative standard deviation of about 10%, making it far too lengthy and inaccurate for quick adjustments to the cement-making process. X-ray fluorescence (XRF) can only be used to measure the total Ca content in a sample - the different phases or compounds of Ca, such as C2S or C3S, cannot be separated. Concentrations of the latter are usually measured

using the X-ray diffraction (XRD) technique. For cement plants in which free-lime analysis only is needed for process control, the S8 LION spectrometer with simultaneous wavelength dispersive X-ray fluorescence (WDXRF) offers a free-lime channel based on the XRD technique. This XRD free-lime channel, which complements the S8 LION's element channels, enables the elemental composition and free-lime content to be quickly and precisely determined from the same process sample in one run.

This report outlines the analytical performance of the S8 LION in free-lime determination for the monitoring and optimizing of the cement-making process.

Instrument

Specially designed for quality and process control in cement manufacturing, mining and the processing of industrial minerals, the S8 LION is an industry grade system: reliability of operation and thus a high instrument uptime, short time-to-result and high precision, enabling immediate feedback and quick adjustment of the process.

The concentration of elements and free lime in clinker is measured using pressed pellets. Employing SampleCareTM technology with a sample loader and tube-above geometry,

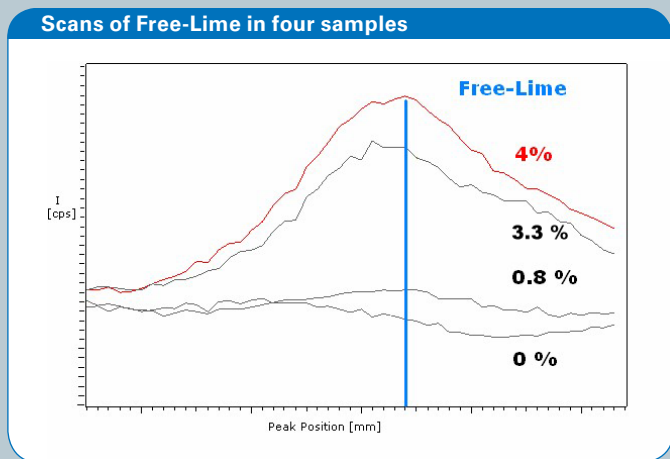


Figure 1: Scans of four different clinker samples with concentrations ranging from 0 – 4%.

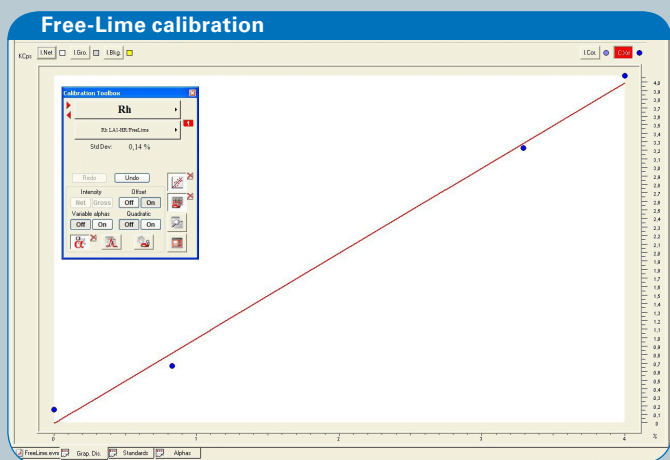


Figure 2: Calibration curve of free-lime in clinker based on the S8 LION

the S8 LION handles the pellets with care and therefore is not affected by dust and debris resulting from pellet breakage. The sample loader with its swing arm and sample-lifting device ensures optimum presentation of the sample.

Owing to accurate positioning of the sample surface, the temperature control adjusted to each crystal, the temperature-stabilized enclosure and the constant vacuum, a high analytical precision is achieved even for the light elements.

Of course the spectrometer enclosure of the S8 LION is sealed against dust to ensure maximum instrument uptime even under harsh conditions. Regular PCs with a keyboard, a mouse and displays will not withstand these conditions. Thanks to the unique TouchControl™ interface, in harsh environments the S8 LION can be operated in island mode, that is, without a PC. Added to this, starting of samples via TouchControl™ is simple, intuitive and failsafe, which leads to improved productivity. All this makes the S8 LION ideal for a production control environment.

For elemental analysis and the quantification of free lime by XRD, the S8 LION can have up to 13 element channels plus one free-lime channel (XRD) to cover all analytical tasks for raw mix, clinker and cement control. Each channel is optimized for the specific element and its concentration range.

Sample preparation

All samples were prepared as pressed pellets in 51.5 mm steel rings using the sample preparation device APM (Automatic Press and Mill) from Polysius. For grinding, two grinding-aid tablets were added to the clinker. The final pellets were pressed under a weight of 5 tons.

Measurement

Measurements were performed on the S8 LION with simultaneous WDXRF with a free-lime channel. The S8 LION for rapid free-lime quantification in clinker samples for process control is equipped with 10 channels for the elements Na, Mg, Al, Si, P, S, K, Ca, Ti, Fe and the free lime channel (XRD). A 4KW Rh target X-ray tube was used. The integration time for free lime was 60 seconds.

Results

To calibrate the S8 LION for free-lime determination, standard samples with concentrations ranging from 0 – 4% were used.

The results were verified with TOPAS Rietveld analysis using a dataset from the D4 ENDEAVOR. The scans of four different samples are shown in figure 1.

Owing to the use of Rh radiation, the scattered radiation and sample fluorescence is very low, resulting in a reduced

Table 1: Calibration data for free-lime

Standard Name	Chemical Concentration [%]	XRD Concentration [%]	LLD (PPM)
FL-Std 1	Trace	0.15	90
FL-Std 2	0.83	0.69	90
FL-Std 3	3.29	3.22	90
FL-Std 4	4.00	4.07	90

One clinker sample was analyzed 10 times to test the reproducibility of the free-lime channel. The results are summarized in table 2. The S8 LION achieves an absolute standard deviation of 0.013% for one sample containing 0.75%

Table 2: Reproducibility of free-lime in clinker for low concentration levels by running two samples alternated 10 times.

Time	Sample 1 Free-Lime (%)	Sample 2 Free-Lime (%)
1	0.76	2.90
2	0.78	2.93
3	0.74	2.89
4	0.76	2.89
5	0.76	2.96
6	0.75	2.92
7	0.74	2.97
8	0.76	2.93
9	0.74	2.95
10	0.75	2.97
Average	0.75	2.93
Abs. Std. Dev.	0.013	0.03
Rel. Std. Dev.	1,73	1.05

background. It is evident from the scans that the S8 LION is the right tool for measuring free lime in process samples from 0.1 % upwards.

One clinker sample was analyzed 10 times to test the reproducibility of the free-lime channel. The results are summarized in table 2. The S8 LION achieves an absolute standard deviation of 0.013% for one sample with a free-lime content of 0.75%.

The free-lime channel was calibrated on the basis of the four standard samples. The calibration curve is shown in figure 2; the details of the calibration are listed in table 1. The standard deviation of the regression is 0.14%. The resulting LLD for free lime is 90 ppm.

Conclusions

The S8 LION with a free-lime channel provides accurate and reproducible quantification of the free-lime concentration in

clinker and cement samples covering the concentration range required for process control. The excellent free lime data can be used to monitor and adjust the kiln process and to achieve considerable fuel savings.

Combining elemental analysis by simultaneous XRF and the free-lime channel based on XRD technology in one instrument allows all basic process parameters to be monitored under the same conditions with a single sample in one run. This reduces handling time as well as time spent on sample preparation and instrumentation. Since the S8 LION is designed for reliability and allows maximum uptime and precision to be achieved, it is the perfect industrial analytical system for PC/QC in cement plants.

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