Quick-fire laser analysis

Cement plants rely on rapid analysis of clinker to monitor free lime levels and therefore, avoid a deterioration of clinker quality. To support this need for quick but accurate results, a new real-time analysis method has been developed, using laser-induced breakdown spectroscopy.

■ *by **Dr Alexander Baryshnikov and Dr Mindaugas Dailide**, Lyncis, Lithuania*

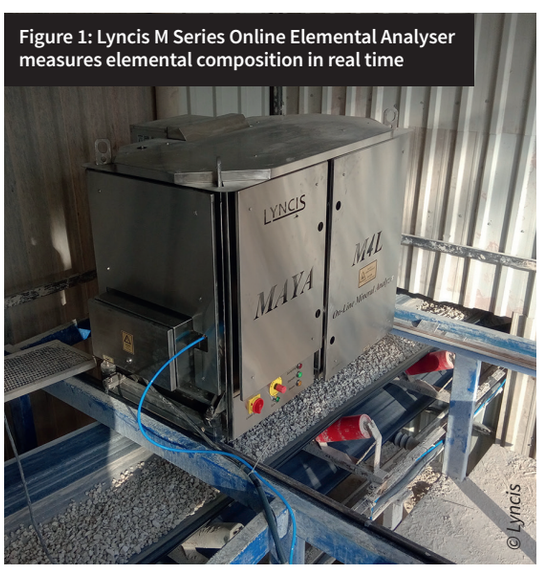
An excess of free lime (f.CaO) has adverse effects on clinker quality. Therefore, to maintain a high clinker quality cement plants continuously check free lime levels in the production process. However, current monitoring methods rely on the periodical collection of samples and subsequent analysis in the plant's laboratory using wet chemistry or X-ray diffractometry (XRD) techniques, which leads to a delay between sampling and receiving test results. This delay prevents the timely adjustment of kiln conditions, proper preparation of the raw mill and stabilisation of the f.CaO residue, leading to potential quality issues and higher energy consumption. To enable a faster and more accurate analysis, a novel real-time method using laser-induced breakdown spectroscopy (LIBS) was developed by Lyncis at its facility in Lithuania.

LIBS description

LIBS is a radiation-free analysis technique that can measure elemental composition in real time using the Lyncis M Series Online Elemental Analyser (see Figure 1).

The pulses of the laser beam are directly delivered onto the material on the conveyor or in the slurry stream. Each pulse generates plasma from the material. When the plasma cools down, it emits light that contains information on the elemental composition of the analysed material. Each element has a specific fingerprint-like set of signals in the LIBS spectrum that allows for the identification of all elements in one measurement (see Figure 2).

Figure 1: Lyncis M Series Online Elemental Analyser measures elemental composition in real time



Testing LIBS accuracy

LIBS technology proved to be very universal as Lyncis has successfully implemented it in various industries and materials around the globe since 2008.

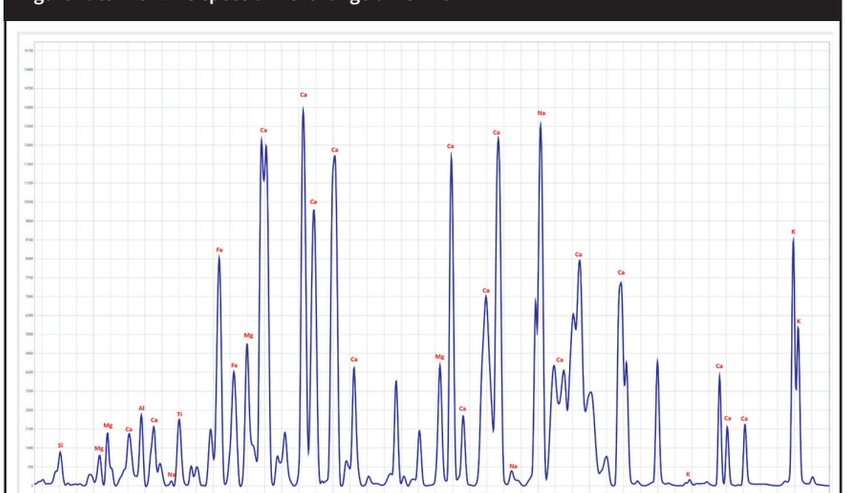
For example, a set of clinker samples was collected from a cement production line in the USA. The samples were analysed with an M Series Online Elemental Analyser, based on LIBS technology.

To test the accuracy of LIBS technology, the samples were kept in their original state and granulometry without any processing or sample preparation and analysed on a moving conveyor to simulate conditions in the cement plant.

The comparison of f.CaO online analysis with laboratory analysis resulted in R^2 = 0.918, RMSD = 0.1 per cent and a relative error of 6.4 per cent (see Figure 3). Such accuracy is sufficiently high for monitoring the f.CaO trend on the production conveyor system and adjusting the process parameters influencing the concentration of f.CaO in real-time, eliminating the delay caused by sample collection, preparation and analysis in the laboratory.

Further comparison of online analysis with laboratory analysis of the CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, Mn_2O_5 and SrO elemental oxides showed the accuracy in the range of R^2 = 0.79-0.94, RMSD = 0.001-0.16 per cent and relative error of 7.8-12.5 per cent in the concentration ranges typical for clinker, demonstrating the suitability of online LIBS technology to measure these elements.

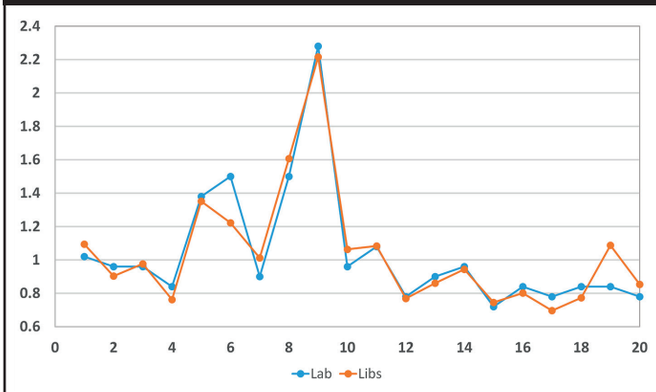
Figure 2: clinker LIBS spectra in the range of 234-792nm



Source: Lyncis

In addition, clinker compositional parameters were measured and compared with the laboratory results. The accuracy of LF, SR, A/F, C_3S, C_2S, C_3A, C_4AF, $CaSO_4$, LSF, liquid (per cent), burnability index, SO_3/Alk and NaEq was in the range R^2 = 0.81-0.92, RMSD = 0.006-1.04 per cent and a relative error of 6.2-10.9 per cent, demonstrating the suitability of online LIBS method for evaluating clinker composition. It is worth mentioning, that compositional parameters were not calculated using elemental analysis data but measured directly by processing spectral data.

Figure 3: comparison of online LIBS analyser and laboratory analysis of clinker free lime (f.CaO)



Source: Lyncis

Samples with reduced particle size

The capabilities of the LIBS analyser were also evaluated to analyse clinker samples with a particle size reduced to ~3mm. The analysis was carried out on the moving conveyor to simulate conditions in a cement plant.

The comparison of LIBS online analyser results with the laboratory results for f.CaO resulted in R^2 = 0.95, RMSD = 0.08 per cent and a relative error of 4.9 per cent. For the analysis in terms of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3, Na_2O, K_2O, TiO_2, P_2O_5, Mn_2O_5 and SrO the result was R^2 = 0.85-0.96, RMSD = 0.0005-0.11 per cent and a relative error of 5.0-9.5 per cent.

For LF, SR, A/F, C_3S, C_2S, C_3A, C_4AF, $CaSO_4$, LSF, liquid (per cent), burnability index, SO_3/Alk and NaEq the measurement accuracy was in the range R^2 = 0.84-0.96, RMSD = 0.004-0.58 per cent and a relative error of 5.4-11.8 per cent. The accuracy for most of the elements and parameters was slightly higher for samples with the reduced particle size, indicating that in the cases where higher accuracy is important it is recommended that a set-up with a bypass conveyor and flow-through mill is installed.

Eliminating costly delays

LIBS is real-time analysis method of free lime in clinker developed to eliminate the delay caused by sample collection, preparation and analysis in the laboratory. This capability to optimise kiln conditions using real-time f.CaO and other parameters has the potential to significantly reduce energy consumption and eliminate quality issues. ■