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CEMENT ANALYSIS – *A Time Critical Solution*

**NEAL ROBSON,
OXFORD INSTRUMENTS, UK,
INTRODUCES COST-EFFECTIVE,
BENCHTOP XRF ANALYSIS.**

In today's cement manufacturing process the critical issues facing production are to increase output and minimise costs while improving quality. From the quarrying of raw materials to the shipping of finished product, time-dependent analysis is required in order to maintain integrity and smooth running. Ensuring that chemical specifications are met at each key stage will result in a consistent and predictable product, thus allowing time and cost optimisation.

XRF analysis is a commonly accepted technique for the analysis of the raw materials, intermediate and finished products offering simplicity of sample preparation, speed and accuracy of analysis.

Benchtop 'next generation' XRF instruments, such as the X-Supreme8000, now provide a low cost solution for continuous product quality. They offer high performance analysis with field proven high reliability, and are often operated by production staff on a 24/7 basis. These systems



Figure 1. Benchtop XRF analyser.

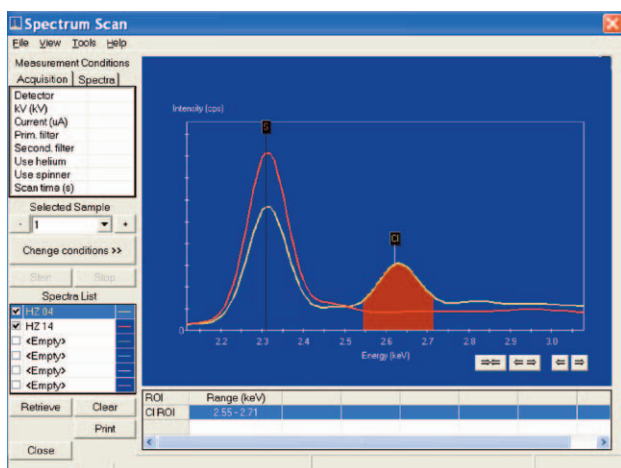


Figure 2. Two superimposed X-ray spectra of cement samples with an X-ray Region of Interest (ROI) for Cl, covering the X-ray energy range 2.55 – 2.71 keV.



Figure 3. Standard 40 mm sample holder with cement pellet in place.

can be used both to measure the main elements (magnesium, aluminium, silicon, calcium and iron) in cement making materials at key points in the production process and as a backup to another XRF system. Used either as a stand-alone or as part of an automation system, XRF instruments ensure conformance to any ISO specification that requires compliance with 24/7 continuous product analysis.

XRF instrumentation

The cement industry accepts and respects X-ray spectrometry as an analytical technique. Instruments fall into two broad categories: Wavelength Dispersive (WDXRF) and benchtop Energy Dispersive spectrometers (EDXRF).

Benchtop EDXRF systems are small, low cost, single sample (e.g. Lab-X3500) or multi-sample (e.g. the X-Supreme8000 shown in Figure 1) instruments that are easy to install and are often situated in a variety of locations, i.e. in a quarry, blending site, grinding plant, at-line, control room or in the laboratory. They are normally operated by production shift personnel giving a simple cost-effective solution to time critical analysis.

The latest generation of EDXRF instruments now offer a field proven robust and reliable solution. They employ matched X-ray tube and solid state high resolution, and high count-rate detectors for the elemental determination of low atomic number elements such as sodium in cement and chlorine in clinker, as well as the standard range of cement making elements, including Mg, Al, Si, S, K, Ca and Fe.

Principle of operation

XRF occurs when elements in a sample are excited at an atomic level. As they return to their initial state they emit a characteristic X-ray photon. Each element emits a unique X-ray energy so an XRF spectrometer consists of a source of excitation and selective detection and quantification of the characteristic elemental X-ray photons. A calibration line is then used to perform quantitative analysis.

Close attention to detail has produced EDXRF instrumentation that ensures successful cement analysis. Examples include the use of low power, high efficiency X-ray tubes for elemental excitation. One advantage of this method is that X-ray tubes are only switched on when taking a measurement that leads to minimal heat generation with no requirement for external cooling. This results in highly stable, reliable X-ray tubes with long lifetimes, typically greater than ten years. The low running and maintenance costs are another benefit, giving an overall low cost of ownership.

Detection of the characteristic X-rays is accomplished using the latest detection technology: a Silicon Drift Detector (SDD) providing high spectral resolution. The combination of selective elemental excitation with optimum detection results in optimal speed of analysis and stable and reliable results.

Since dust ingress is a major factor in the lifespan of instrumentation, the design of the X-Supreme means that cooling air is circulated in a separate compartment – a ‘wind tunnel’ – from the main spectrometer components. This feature, combined with the integral industrial grade PC, which does not use fans, ensures a long operating life for the main hard disk and spectrometer.

An example of the X-ray spectrum that results from using this combination to measure Cl in clinker is shown in Figure 2. In this example two spectra are displayed,

representing 0.014% Cl (red spectra) and 0.51% Cl (yellow spectra) in cement. This example demonstrates that a good elemental separation from adjacent elements in the periodic table, in this case S and Cl, can now be achieved, leading to low detection limits (Table 1).

Sample preparation

In routine production control, samples are often measured as pressed pellets: the powder sample is first ground in a swing mill to ensure a consistent particle size, and then compressed using a hydraulic press at 20 t to produce a strong pellet. A 40 mm sample holder then holds the pressed pellet (Figure 3).

In some cases an automatic sample preparation system is used where the pressed pellet is often retained in a steel ring (Polysius type) measuring 51.5 mm dia. (2 in.). In this instance, a special magnetic holder is used to load the sample onto the sample carousel of the instrument (Figure 4). In both examples the sample is rotated during the measurement in order to minimise any sample inhomogeneity.

This method is particularly effective during periods when the main XRF is unavailable, thus allowing analysis to continue. This has major benefits, as it not only prevents any interruptions to the production process, but it also means that ISO criteria on continuous testing will be met.

Performance and results

For high quality production control the instrument is first calibrated, which involves measuring a range of well analysed samples of known elemental content. In the determination

of Cl in cement, an X-ray 'Region of Interest' (ROI) is defined around the Cl peak and the resulting X-ray intensity is obtained for each calibration standard measured. The calibration (after X-ray corrections have been applied) is shown in Figure 5. For a comprehensive cement analysis, the data in Table 2 shows the performance for the remaining cement elements. In addition, from the X-Supreme8000's instrument repeatability, it can be seen to comply with the precision requirements of the ASTM C114: 'Standard methods of chemical analysis of hydraulic cement'.

Quality control

One strategy that ensures the spectrometer remains within specifications over the long-term is regular measurement of



Figure 4. Pressed cement pellets in 51.5 mm (2 in.) steel rings are loaded into the magnetic holder and placed onto the 10-position sample carousel of the X-Supreme8000 instrument.

Analyte	Range (% m/m)	Standard error of calibration (% m/m)	Guaranteed limit of detection (3σ) (% m/m)	Mid-range precision (95% confidence) (% m/m)	Measurement time (seconds)*
Cl	0.014 – 0.51	0.006	0.005	0.0035	200

* The measurement time is a simultaneous time measuring Na, Mg, Al, Si, S and Cl.

Analyte	Range (% m/m)	Standard error of calibration (% m/m)	Guaranteed limit of detection (3σ) (% m/m)	Mid-range precision (95% confidence) (% m/m)	Measurement time (minutes)
Na ₂ O	0.02 – 1.07	0.04	0.021	0.012	~ 7
MgO	0.81 – 4.48	0.06	0.015	0.03	
Al ₂ O ₃	3.9 – 7.1	0.1	n/a	0.03	
SiO ₂	18.6 – 22.4	0.2	n/a	0.07	
P ₂ O ₅	0.02 – 0.31	0.009	0.005	0.003	
SO ₃	2.1 – 4.6	0.1	n/a	0.011	
K ₂ O	0.09 – 1.23	0.04	0.005	0.011	
CaO	57.6 – 67.9	0.5	n/a	0.08	
TiO ₂	0.08 – 0.37	0.006	0.003	0.004	
Cr ₂ O ₃	0.002 – 0.06	0.003	0.001	0.001	
Mn ₂ O ₃	0.007 – 0.26	0.006	0.001	0.002	
Fe ₂ O ₃	0.15 – 3.1	0.06	0.003	0.008	
ZnO	0.001 – 0.11	0.001	0.0006	0.001	
SrO	0.02 – 0.64	0.004	0.002	0.001	

The precision was calculated from 10 repeat measurements of NIST standards. The standards were chosen so that the analytes' concentration matches the calibration mid-range.

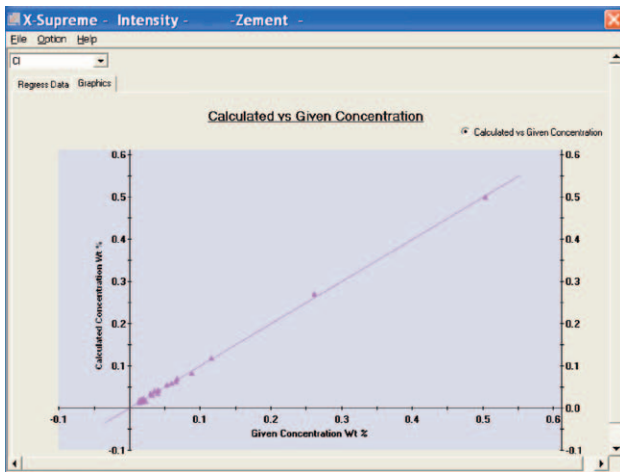


Figure 5. Calibration regression for Cl in cement.

Sample/ Batch2	Zement
Analyte	Concentration
SiO2	23.03 Wt %
Fe2O3	1.90 Wt %
Al2O3	6.48 Wt %
CaO	54.46 Wt %
MgO	2.76 Wt %
SO3	4.25 Wt %
K2O	0.68 Wt %
Na2O	0.09 Wt %
TiO2	0.73 Wt %
MnO	0.201 Wt %
Cr2O3	0.0068 Wt %
P2O5	0.37 Wt %
Cl	0.016 Wt %
AR	3.41 No Units
SR	2.75 No Units
LSF	98.17 No Units

Figure 6. Results and cement calculations displayed on the X-Supreme8000.

a quality control (QC) sample. If the QC sample results are within customer-defined specifications, no further action is required. Correction (restandardisation) is only required if the QC sample is outside specification.

The latest generation of EDXRF instruments have inherent stability, typically meaning that restandardisation is required infrequently. When it is required, it involves the simple measurement of a few ‘Setting Up Samples’ (SUS), which are provided with the instrument, and after measurement redefines the instrument performance. A full new calibration is typically only performed every 12 – 18 months. This is because an ISO procedure specifies a maximum time limit before a full calibration is accomplished, not because the SUS cannot compensate for any slight change in long-term instrument performance.

Routine analysis

On a 24/7 basis, production staff can load from one to ten samples onto the sample carousel; enter the sample data either by mouse, bar code reader, or touch screen; and the measurement starts. For a single measurement (in simultaneous analysis mode), provisional results on key elements are displayed after just 5 seconds of

measurement. This gives a rapid assessment of elemental content, allowing confirmation of product quality.

If multi-samples are being measured, the red/yellow/green labels for each sample show those samples already measured and those awaiting analysis.

At the end of each measurement, customer-specified ‘cement moduli calculations’ are also performed on the final result. Examples include lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR), and these are calculated and displayed at the end of each measurement, allowing optimisation of the production process (Figure 6).

Additional software

In addition to the elemental concentrations and cement moduli, a software program called SMARTCHECK allows one or a series of ‘logic calculations’ to be performed on the final results. The output from the program can be instructions to the production staff on optimisation of the production process. The program can be applied to the value of the LSF. As an example, the specification for clinker could be 90 – 92, so the manager would specify a SMARTCHECK calculation to ensure that every clinker sample measured has an LSF between these values. If the production is within tolerance then no warning message will be displayed. However, if a result is outside the tolerance, then a customer-defined warning message can be displayed alerting the production operator to a potential problem. These checks can be applied to individual elements, ratios and calculations, etc. In all cases, this level of checking on key cement process parameters ensures that continued high quality analysis is carried out by production staff.

Data storage and output

Once the results are accepted, they can be printed and/or stored as specified by the manager in the analytical method. Results can be accessed remotely by other PC-based systems for subsequent data storage or as part of a centralised quality control system.

Remote diagnostics

In addition to the inherent high reliability of EDXRF, remote diagnostics can be performed, allowing an ongoing health check, using in-built samples located underneath the sample carousel. This aid to preventive maintenance ensures the instrument is continuing to perform to specification. Any servicing requiring additional parts is then readily available to minimise downtime.

Conclusion

Cost-effective XRF analysis with field proven reliability can now be achieved with instruments located on or near a production site, and operated by production staff giving 24/7 analysis coverage, ensuring consistent product quality. 🌐

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