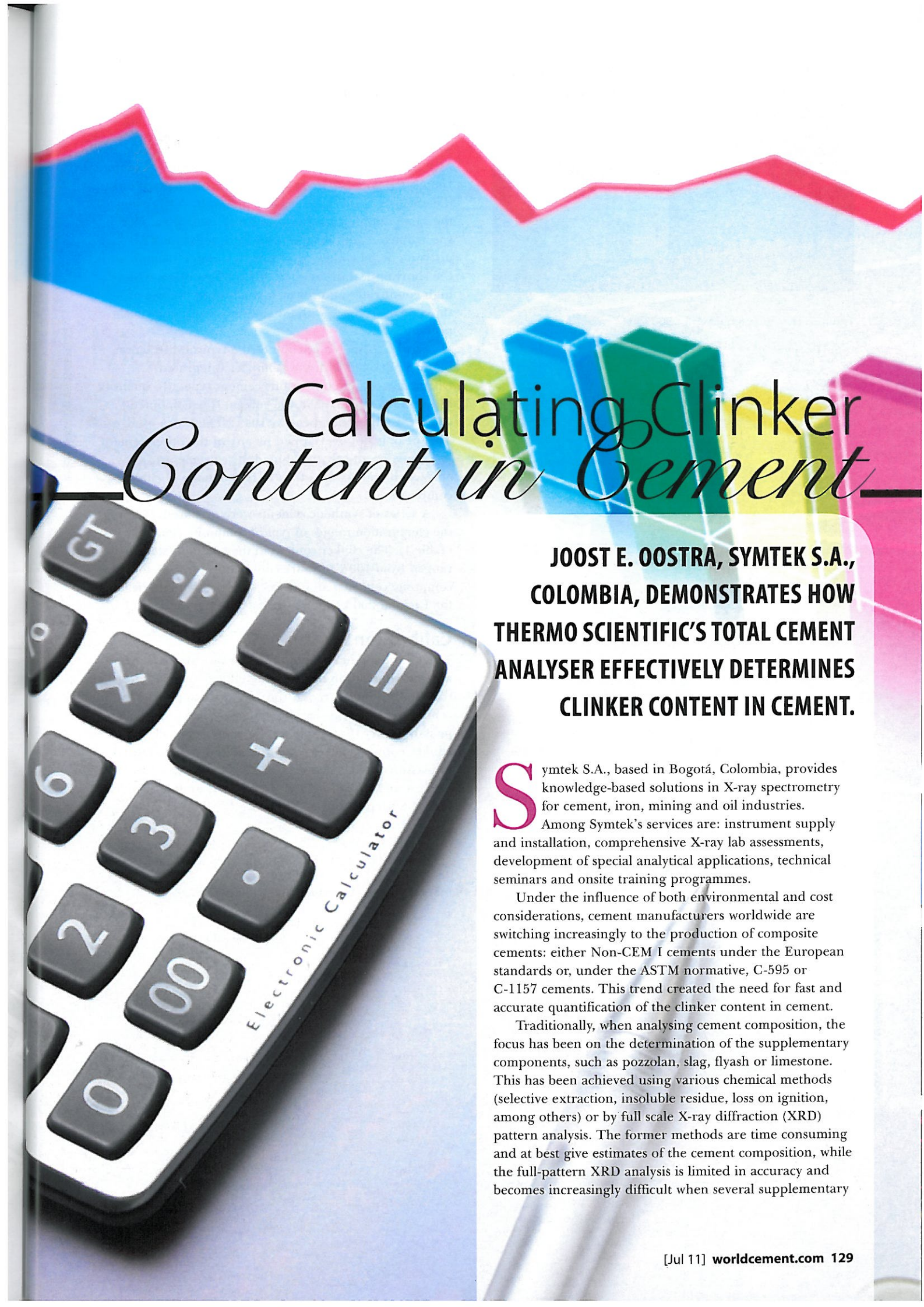
Calculating Clinker Content in Cement



JOOST E. OOSTRA, SYMTEK S.A., COLOMBIA, DEMONSTRATES HOW THERMO SCIENTIFIC'S TOTAL CEMENT ANALYSER EFFECTIVELY DETERMINES CLINKER CONTENT IN CEMENT.

Symtek S.A., based in Bogotá, Colombia, provides knowledge-based solutions in X-ray spectrometry for cement, iron, mining and oil industries. Among Symtek's services are: instrument supply and installation, comprehensive X-ray lab assessments, development of special analytical applications, technical seminars and onsite training programmes.

Under the influence of both environmental and cost considerations, cement manufacturers worldwide are switching increasingly to the production of composite cements: either Non-CEM I cements under the European standards or, under the ASTM normative, C-595 or C-1157 cements. This trend created the need for fast and accurate quantification of the clinker content in cement.

Traditionally, when analysing cement composition, the focus has been on the determination of the supplementary components, such as pozzolan, slag, flyash or limestone. This has been achieved using various chemical methods (selective extraction, insoluble residue, loss on ignition, among others) or by full scale X-ray diffraction (XRD) pattern analysis. The former methods are time consuming and at best give estimates of the cement composition, while the full-pattern XRD analysis is limited in accuracy and becomes increasingly difficult when several supplementary

Figure 1. Thermo Scientific ARL 9900 Total Cement Analyser.

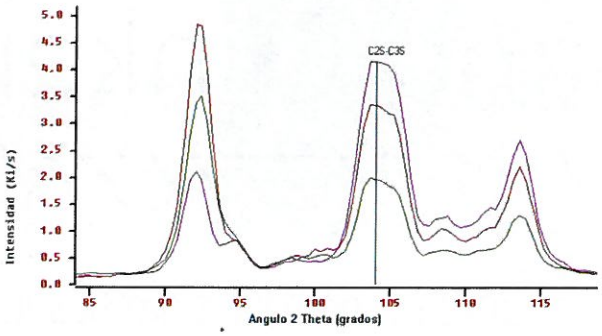


Figure 2. XRD scans of pure clinker and two composite cements.

materials are simultaneously present in the cement. To compound the difficulties, some supplementary cementitious materials, such as pozzolans, exhibit a wide variation in chemical and mineralogical composition. However, since clinker is usually the most expensive component in the cement formulation, it is desirable to measure its content directly and with the highest possible accuracy.

This article presents the results of a direct XRD calibration developed to quantify the clinker content in composite cement, including several components. The results show that fast and accurate clinker content determination is possible in complex composite cement.

Experimental

The calibration was made using a Thermo Scientific ARL 9900 Total Cement Analyser fitted with its Compact Integrated Diffraction System. This instrument allows the analysis of the main clinker phases by XRD using the same sample chamber and X-ray tube of an XRF spectrometer, without the need for a separate XRD instrument. The analysis of samples under vacuum and the short optical distance of this configuration achieve high count rates and sensitivity, allowing the use of short analysis times without compromising analytical precision.

Figure 2 shows a portion of the typical diffraction pattern obtained with the Compact Integrated Diffraction System on various cement types. To quantify the amount of clinker in the cement, the combined C_3S – C_2S diffraction peak at 104° 2-Theta was used. This peak is not overlapped by any of the other cement constituents, and the combined measurement of C_3S and C_2S dampens the effect of fluctuations in clinker composition.

A series of synthetic cements were prepared, covering the composition ranges of typical composite cements (Table 1). The clinker content in these various standards ranged from 100% for pure clinker down to 50% for some composite cements. All samples were pressed into pellets for 1 min at 200 kN pressure.

Calibration

The samples containing no blastfurnace slag exhibited a linear correlation between the clinker content and the intensity measured at the 104° 2-theta peak. The cements containing slag, however, showed higher peak intensity than expected for their particular clinker content. This is due to the amorphous nature of blastfurnace slag, which increases the diffraction background radiation across the whole angular range. Hence a correction was introduced and an excellent

Table 1. Composition ranges used in calibration (%)

Standard	Clinker	Natural pozzolan	Blastfurnace slag	Limestone	Gypsum
1	100	0	0	0	0
2	90	0	0	0	10
3	80	10	0	5	5
4	80	15	0	0	5
5	70	20	0	5	5
6	60	25	0	10	5
7	55	30	0	10	5
8	50	35	0	10	5
9	50	20	20	5	5
10	50	0	40	5	5
11	60	15	15	5	5
12	60	0	30	5	5

These synthetic standards were analysed in the spectrometer at 30 kV and 80 mA (2400 W), using 60 sec analysis time.

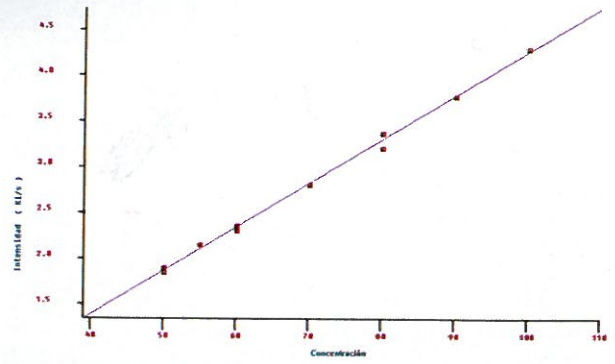


Figure 3. Clinker content calibration after correction.

correlation was obtained, as can be seen in Figure 3. The Standard Estimate Error (SEE) of the calibration was 0.9% clinker content.

In order to correct for instrumental drift and for future changes in clinker quality, the calibration was referenced to a pure clinker sample allowing periodical standardisation of the results.

In addition to the calibration for clinker content, it is also often possible to set up calibrations for each of the supplementary components of the cements. In this case the Thermo Scientific ARL 9900 Total Cement Analyser can provide fast and reliable information on the total composition of the mill product. Apart from the quality control and cost optimisation of the cement, this information provides the plant with a continuous and independent monitoring of the weighing scales and the material feed to the mill.

Measurement time

Due to the analysis under vacuum and the use of the close-coupled Compact Integrated XRD system, very high counting intensities are obtained, resulting in a statistical counting error of less than 0.01% clinker content. As the whole analysis time is usefully spent measuring the C_3S – C_2S peak of interest rather than scanning a wide angular range, this adds to the high counting intensities obtained. An analysis time of 60 sec was used for calibration purposes, but the data shows that for routine analysis, this can be reduced to 10 sec without loss of result quality.

Conclusion

Using the Thermo Scientific ARL 9900 Total Cement Analyser, fast and direct determination of clinker content in cement is possible, with better accuracy than has been previously attained by traditional methods. The short response time and repeatability of results provide a valuable tool for process control and quality optimisation. In this way, XRD analysis technology enables the cement producer to push the limits of addition of alternative cementitious materials, lower CO_2 emissions and widen the selection of special cements available to the end user.