MAKING THE RIGHT CHOICE

Geoffroy Bultynck, HeidelbergCement CBR-Plant, Belgium, Michael Principato, HeidelbergCement Technology Center, Germany, and Ravi Yellepeddi and Didier Bonvin, Thermo Electron SA, Switzerland, present a case study that illustrates how the analytical needs in a cement plant can be matched to the wide range of X-ray solutions available.

Introduction

A variety of X-ray fluorescence (XRF) and X-ray diffraction (XRD) instruments are available to the cement industry today. From bench top energy dispersive XRF systems to stand-alone wavelength dispersive XRF and Integrated XRF-XRD systems, cement laboratories have a significant choice from which to find a match for their analytical needs. In the past, this choice mainly depended upon the inherent parameters of a specific cement plant in terms of its raw materials, process control, additives use, types of cement and overall capacity. Now, one has to take into account the analytical needs generated by other issues, such as the use of alternate fuels, control of environmental effects, regulatory requirements, optimisation of cement quality with reference to the end-user application and total cost of ownership per analysis.

Indeed, the cement industry has come a long way in exploiting XRF capabilities for the chemical analysis of all kinds of materials beyond the basic oxides. In addition, on-line implementation of the X-ray diffraction technique as a routine tool for the analysis of free lime, clinker phases and additives in cement is becoming more practical and reliable. It is therefore clear that most cement plants are taking an integrated approach where the analytical needs of a cement plant are evaluated as a function of XRF and XRD capabilities and the available expertise.

This case study details results from a recent investigation that led to the selection of a particular X-ray instrument. Typical data from these tests are produced here to illustrate the process. The examples cited actually cover the entire cement process: characterisation of raw materials, control of the clinker phases and quantification of additives in cement.

Experimental process

An ARL 9900 XP Total Cement Analyser (Figure 1) from Thermo Electron Corporation has been used for these tests. This instrument integrates a series of XRF Fixed Channels (Monochromators), for simultaneous analysis of various oxides, XRF Goniometer, which offers flexibility to cover more elements/oxides cost effectively, and a patented integrated XRD system for phase analysis. The instrument uses one X-ray tube with the same kV and mA conditions to perform

Figure 1. ARL 9900 XP Total Cement Analyser.

both XRF and XRD measurements on the same sample. Sample preparation (grinding and pelletizing) can be optimised in order to obtain uncompromised XRF and XRD data. Both XRF and XRD are done under vacuum with highly reproducible sample positioning and measurement conditions. Also, the same software is used for data acquisition and data processing through calibrations for a truly quantitative analysis. The final report covers the complete analysis of oxides in conjunction with their corresponding phases of importance and utility.

The ARL 9900 Series can also be integrated into process control using fully automated sample preparation, sample transport and result transmission modules.

Table 1. Comparative data for Cr in synthetic standards

Std. nr.	Concentration Cr (ppm) calculated	Concentration Cr (ppm) by colorimetry	Cr (ppm) XRF
1	2.3	2.3	2.5
2	6.4	4.3	7.4
3	10.5	10	10.7
4	14.6	13	13.7
5	18.7	17.2	18.7
6	22.8	21.2	22
7	26.9	26	26
8	31.06	30.2	30.7
9	35.2	35.5	37
10	39.3	38.8	39.8
11	43.4	43.4	43.4
12	-	46	43.3

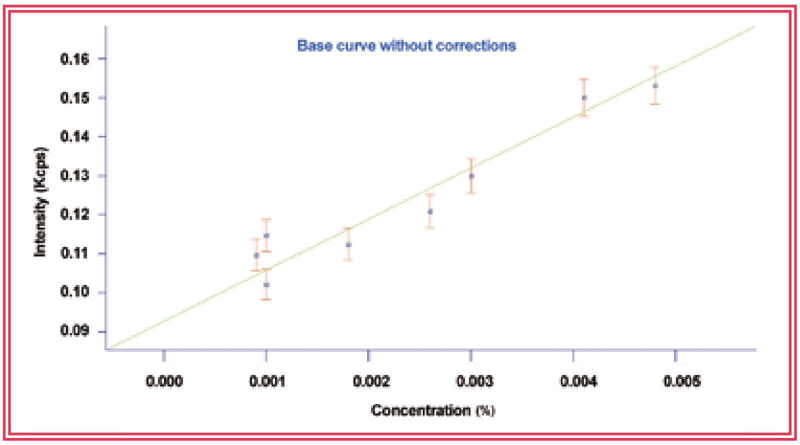

Figure 2. Calibration curve for Cr in a series of cement related materials.

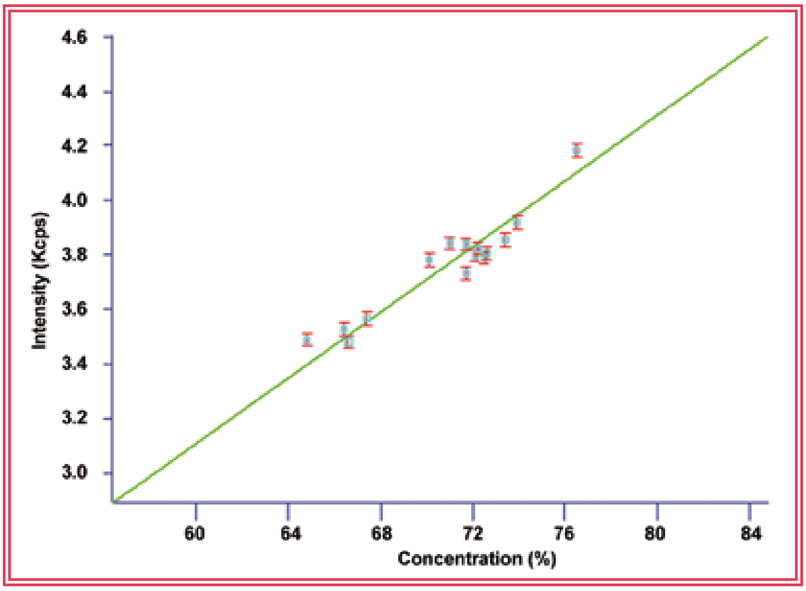

Figure 3. Alite calibration curve using integrated XRD system.

Results and discussion

Analysis of trace levels of chromium in limestone using XRF

It is common practice to use XRF to analyse the major and minor oxides in raw materials such as limestone, clay, iron ore, bauxite etc. prior to their blending into raw meal. For example, using a pellet of limestone, XRF analysis is performed for the total CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, P_2O_5, MnO and TiO_2 contents. Depending on the origin of this limestone, one can expect to see some of the oxides such as TiO_2 down to 100 ppm level.

HeidelbergCement's Harmignies Works in Belgium produces white cement. Its chromium (Cr) content has to be monitored and controlled because high or varying levels of Cr modify the colour of the cement products.

In order to validate the sensitivity of the X-ray instrument for analysis of Cr, a series of synthetic standards has been prepared by mixing cement with limestone. Their Cr levels have been checked through colorimetry. Table 1 presents the comparative data between calculated Cr levels, colorimetry and XRF results.

The correlation between colorimetry and XRF data is shown in Figure 2. A reasonable calibration curve with the "artificially created" reference samples could be found. It delivers good results even for very low Cr levels. The typical detection limit of around 3 ppm has been obtained, which attests the excellent performance of the instrument.

In order to further ensure that reliable and repeatable performance can be obtained down to trace levels, a repeatability test was performed for Cr analysis. For ten repeat analyses of the same pressed cement pellet containing about 50 ppm of Cr, a standard deviation of 2 ppm or less is obtained with 60 s counting time. This excellent repeatability gives the option to monitor chromium levels in limestone that can range from 2 to 10 ppm. In addition to Cr, iron (Fe) is another critical element for white cement. The performance of the ARL 9900 instrument will enable the producer to control the mix already in the quarry, when materials originate from different quarrying fronts.

Analysis of clinker phases using XRD

There is an increasing interest in quantifying clinker phases in order to monitor their changes during the process. Continuous monitoring of free lime using XRD has been well established. Analysis of Alite, Belite, Aluminate and Ferrite can also be quantified using XRD. While free lime quantification by XRD is established using the traditional wet chemical analysis as a reference method, the quantification of clinker phases is certainly more complicated. It is preferable and almost imperative in some cases to work with true clinker samples from the specific kiln to establish the various parameters for clinker phase quantification. Sample preparation, preferred orientations, granularity and dynamic range are some of the important issues that need to be addressed for an accurate and reliable quantification of clinker phases.

Optical Microscopy counting or Rietveld programs are commonly used in central laboratories to characterise the clinker minerals. Thermo has developed a practical and pragmatic approach based on independent Rietveld analysis of the kiln samples. Indeed, the analytical program called ARL ClinkerQuant™ addresses this important demand from the cement industry.

Figure 3 shows results of ClinkerQuant for the Alite phase in a series of clinker samples from one of HeidelbergCement's plants. Similar calibration curves have been obtained for the remaining three clinker phases: C_2S, C_3A and C_4AF. The accuracy of such quantification essentially reflects the accuracy obtained from Rietveld programs. The reliability of ARL 9900, on the other hand, is superior thanks to high sensitivity (count rates) and highly repeatable measurement accomplished through unique design and integration of the integrated XRD system.

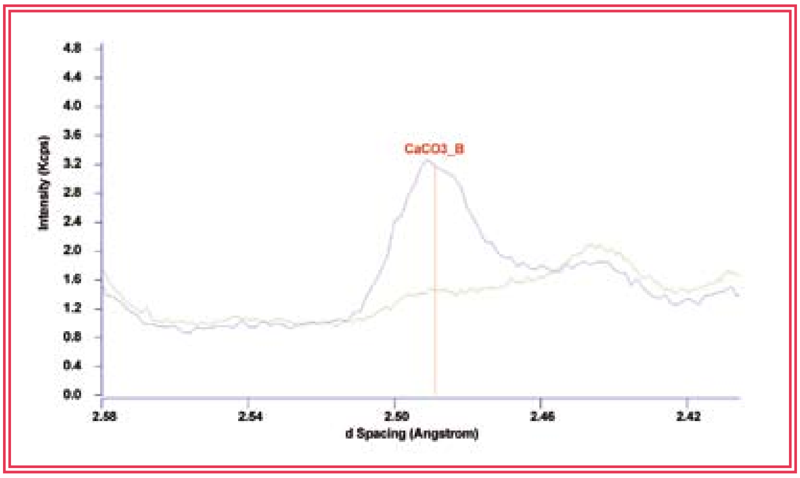

Figure 4. Characteristic XRD peak of $CaCO_3$.

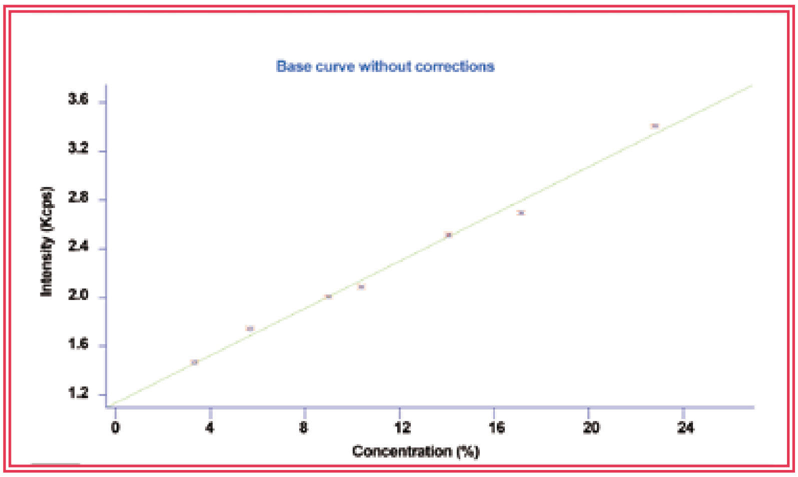

Figure 5. Calibration curve for limestone additions in a series of cement samples.

Analysis of limestone additions in cement using XRD

Once the clinkers are well characterised by the analysis of free lime, clinker phases and overall chemistry, the next step is to assure the quality of the final products. One related issue is the analysis of limestone additions in cement. These additions are subject to the limitations mentioned in the European regulation ENV-197-1 standard. Loss on Ignition (LoI) is commonly used to determine limestone in cement, i.e. through weight loss after calcination. However, this technique is time-consuming and difficult to integrate into a fully automated laboratory. XRD, on the other hand, is most suitable, as it directly determines the $CaCO_3$ additions in cement. Figure 4 shows the characteristic peak of $CaCO_3$ used for this determination. Thanks to the high sensitivity of the integrated XRD in ARL 9900, a well-defined diffraction peak of calcite can be measured and used for quantification.

Figure 5 shows the calibration curve obtained for $CaCO_3$ additions in a series of cement samples. As can be seen, an excellent correlation is obtained between the LoI (CO_2) value and the XRD peak intensity. This calibration curve clearly shows that the Integrated XRD can replace the expensive and time-consuming combustion method to determine limestone additions in cement with good accuracy and precision.

Conclusions

The selection of an X-ray instrument (XRF/XRD) is based on the practical approach of a cement plant towards its well defined analytical needs and their evolution. Given the choice of XRF and XRD instruments available to the cement chemist, it is necessary to evaluate the critical applications from raw materials to the final product in order to take full advantage of the modern instrumentation. In this case study, the Integrated XRF-XRD instrument was found to be the most appropriate choice due to its analytical performance. Prior experience within the HeidelbergCement group regarding reliability and ease of use further supported that decision.

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Bibliography

ENV-197-1 Standard; Cement - Composition, specifications and conformity criteria - Part 1: Common cements.