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APPLICATION NOTE

Determination of limestone addition in cement manufacture

ARL 9900 Series XRF Spectrometer with Compact Integrated XRD System

Key words
ARL 9900, Portland limestone cement, XRF/XRD

Introduction

There is a growing demand and interest in the cement industry to monitor the concentration of limestone, of which calcium carbonate ($CaCO_3$) is the main constituent in the final product, e.g. in Portland limestone cement. Recent regulations' permit the addition of limestone as a filler up to concentration of 30 % depending on the type of cement required. It is therefore important economically to quickly control the concentrations of calcium carbonate in cement in order to guarantee the quality and compliance of the final product.

The X-Ray Diffraction (XRD) technique can analyze specific phases ($CaCO_3$ in this case). In addition, XRD has some advantages because:

- The high energy of the incident radiation means that a larger volume of sample (about 10 times) is measured compared to XRF; this makes the XRD analysis more representative

- Surface contamination, organic binders or grinding aids do not contain the $CaCO_3$ phase and will therefore not alter the limestone analysis.

Instrumentation and samples

The Thermo Scientific ARL 9900 Series consists of a spectrometer that can be fitted with several XRF monochromators for major oxides analysis and a diffraction (XRD) system which has the capability of measuring free lime (CaO), calcite ($CaCO_3$) and quartz phases. In addition, an XRF goniometer can be installed for qualitative or semi-quantitative investigations and sequential analysis of any of 83 elements of the periodic table. Hence, this instrument performs XRF and XRD analysis on the same sample with the same hardware and software environment.

The diffraction system can make qualitative scans and quantitative analysis. This is made possible by using the proven technology of Thermo Fisher Scientific, namely the Moiré fringe positioning mechanisms.

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Since the peak positions and backgrounds in XRD are sensitive to different parameters (e.g. grain size, matrix effects), peak search and peak integration can be done for an accurate analysis. However we have only used peak intensities since no significant peak shifts have been observed in this study.

A series of industrial cement samples classified as grey and white cements as well as finely ground clinkers were used as powders. All samples were pressed at 15 t for 40 s without binder.

Results and discussion

Figure 1 shows the XRD scans on three cement samples containing different concentrations of $CaCO_3$. Two distinct peaks can be identified in each of the scans. The diffraction peak at 2.495 Å is assigned to calcite while the peak at 2.447 Å is attributed to the C_3S phase. The two peaks are well separated enabling quantitative analysis without correction for overlap.
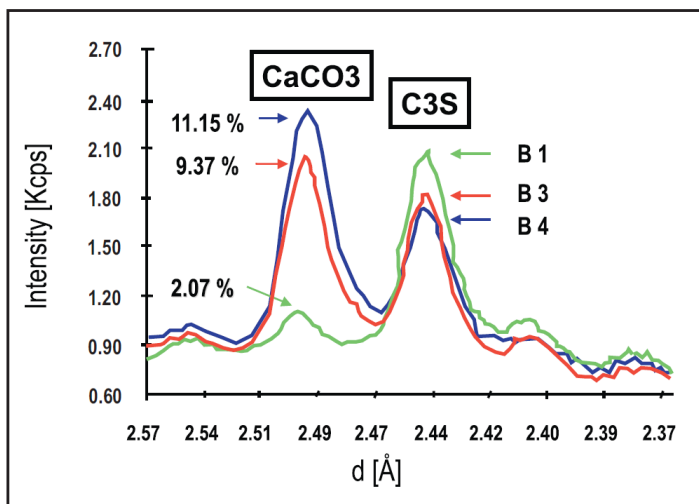

Figure 1: XRD scans on three white cement pellets containing different concentrations of $CaCO_3$.

The regression results using the CaCO3 peak intensity for a set of 8 grey cement standards with the relevant parameters are summarized in Table 1. Figure 2 shows the calibration curve obtained with this set of grey cement standards. A standard error of estimate (SEE) of 0.08% shows the quality of the regression analysis with the Total Cement Analyzer.

Figure 3 presents the calibration curve obtained with a set of 6 white cement and clinker standards with the relevant parameters in Table 3. An SEE of 0.17 % attests the excellent correlation obtained between the nominal concentrations (expressed as CO_2) and the XRD intensities.

Sample	Intensity (KCPS)	Concentration Given (%)	Found (%)	Diff (%)
Cement 1	1.917	7.17	7.23	0.06
Cement 2	1.964	7.55	7.52	-0.03
Cement 3	1.946	7.45	7.41	-0.04
Cement 4	1.044	1.90	1.85	-0.05
Cement 5	1.103	2.07	2.21	0.14
Cement 6	1.077	2.15	2.05	-0.10
Cement 7	0.815	0.45	0.44	-0.01
Cement 8	0.813	0.40	0.42	0.02
Standard error of estimate				0.08
Sensitivity				162 cps/%
Limit of detection (100s)				505 ppm

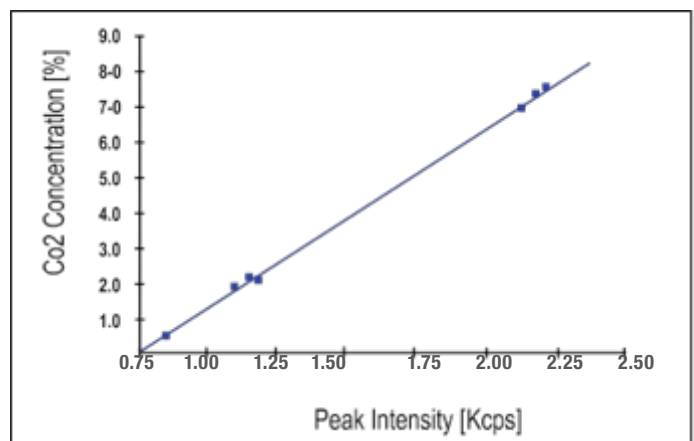Table 1: Regression results on grey Portland cements

Figure 2: Calibration curve obtained using 8 grey Portland cement standards also with peak intensities. Note that $CaCO_3$ peak intensity is used as measured (no background correction).

Sample	Intensity (KCPS)	Concentration Given (%)	Found (%)	Diff (%)
Clinker 1	0.883	0.55	0.73	0.18
Clinker 2	0.890	0.80	0.78	-0.02
Cem B 1	1.062	2.07	2.10	0.03
Cem B 2	1.233	3.65	3.41	-0.24
Cem B 3	2.000	9.37	9.29	-0.08
Cem B 4	2.260	11.15	11.27	0.12
Standard error of estimate				0.17
Sensitivity				131 cps/%
Limit of detection (100s)				645 ppm

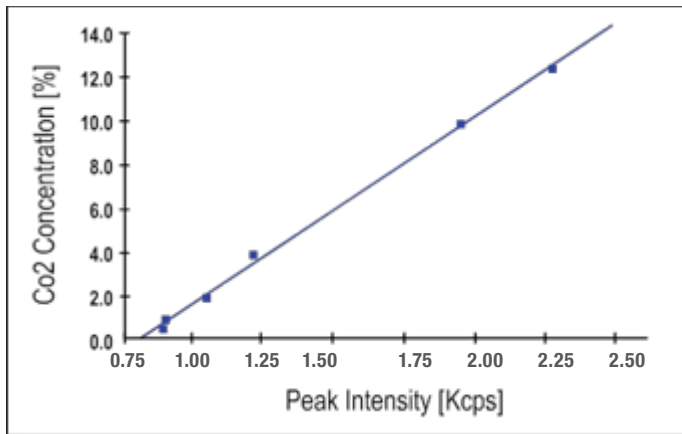Table 2: Regression results on white cements

Figure 3: Calibration curve obtained using 6 white cement and clinker standards. $CaCO_3$ peak intensity is used as measured (no background correction).

Short term and long term stability tests were carried out on sample Cement 3. An average of 21 analyses (each for 100 s) gave the excellent standard deviation of 0.024 % at a level of 7.17 % CO_2 ($CaCO_3$ expressed as CO_2).

Conclusion

These results show that, using the diffraction system integrated into the ARL 9900 can quantify $CaCO_3$ (limestone) in cement with good sensitivity, reliability, and excellent stability. This together with free lime analysis in clinkers shows that monitoring of two major phases needed for quality control in cement plants can be performed using the same integrated diffraction system.

The combination of XRF and XRD in the same instrument can provide complete quality control of clinker and cement, notably of Portland limestone cement. Separate instruments or methods are not required resulting in significant savings from increased operator efficiency and lower running costs.

Notes

The determination of limestone addition could be done using the X-Ray Fluorescence (XRF) technique among other methods. However, XRF analysis is not directly correlated to a phase (e.g. $CaCO_3$). It gives only the total carbon concentration. XRF analysis of carbon (CKα) is also subject to difficulties:

- The fluorescence yield of light elements like carbon is poor, and due to matrix absorption the carbon fluorescence only escapes from a very thin layer at the surface of the sample (about 0.2 micrometer). This means that the volume of sample effectively measured for carbon analysis by XRF is extremely small

- Surface contamination and addition of binding/grinding agents (which are usually organic materials, e.g. stearic acid) can produce inconsistent XRF results due to their carbon content. Binding agents are used to improve the stability of the pellet under vacuum. Hence sample preparation and homogeneity become very important factors in obtaining an accurate analysis of the carbon content using XRF

- When carbon is measured by XRF, all errors are multiplied by a factor of 8 when converting to limestone concentrations.

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