

Determination of Limestone Addition in Cement Manufacture

*ARL 9900 Series with IntelliPower™
Simultaneous-Sequential XRF Spectrometer*

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. Recent European regulations' permit the addition of limestone as a filler up to concentrations of 30 % depending on the type of cement required. It is therefore very important economically to quickly control the concentrations of calcium carbonate in cement in order to guarantee the quality and conformity of the final product.

This can 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 ($\text{CK}\alpha$) 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 μm). 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

On the other hand, the X-Ray Diffraction (XRD) technique is capable of analyzing only a specific phase (CaCO_3 in this case). In addition, XRD intensities are not affected by the factors mentioned above, because:

- The high energy of the incident radiation used allows a larger volume (about 10 times) of sample to be measured than with 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) and calcite (CaCO_3) 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 is capable of making qualitative scans and also quantitative analysis. This is made possible by using the proven technology of Thermo Fisher Scientific, namely the Moiré fringe positioning mechanisms. 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.

Key Words

- ARL 9900
- 3600W
- Cement
- Limestone
- XRF/XRD

Results and discussion

Figure 1 shows the XRD scans on three white 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 2 presents the calibration curve obtained using the CaCO_3 peak intensity in a set of 6 white cement and clinker standards. The regression results are summarized in Table 1. A standard error of estimate (SEE) of 0.17 % attests the excellent correlation obtained between the nominal concentrations (expressed as CO_2) and the XRD intensities.

Figure 3 shows another calibration curve produced with a set of 8 grey cement standards with the relevant parameters in Table 2. Again an SEE of 0.08% shows the quality of the regression and hence that of analysis on the Total Cement Analyzer.

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, CaCO_3 (limestone) can be quantified with:

- Good sensitivity
- Reliability
- Excellent stability of analysis in cements

This together with the previous report on free lime analysis in clinkers clearly 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. Separate instruments or methods are no longer required resulting in significant savings from increased operator efficiency and lower running costs

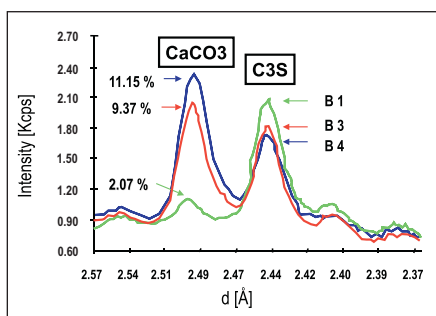


Figure 1: XRD scans on three white cement pellets containing different concentrations of CaCO_3 .

| SAMPLE | INTENSITY [KCPJS] | CONCENTRATIONS | | |
|----------------------------|-------------------|----------------|-----------|-----------|
| | | GIVEN [%] | FOUND [%] | DIFF. [%] |
| Clinker 1 | 0.883 | 0.55 | 0.73 | 0.18 |
| Clinker 2 | 0.890 | 0.80 | 0.78 | -0.02 |
| Cement B 1 | 1.062 | 2.07 | 2.10 | 0.03 |
| Cement B 2 | 1.233 | 3.65 | 3.41 | -0.24 |
| Cement B 3 | 2.000 | 9.37 | 9.29 | -0.08 |
| Cement 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 1: Regression results on white cements

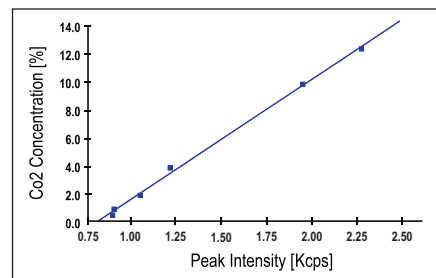


Figure 2: Calibration curve obtained using 6 white cement and clinker standards. Note that CaCO_3 peak intensity is used as measured (no background correction).

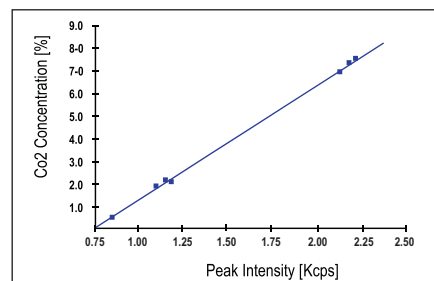


Figure 3: Calibration curve obtained using 8 grey cement standards also with peak intensities.

| SAMPLE | INTENSITY [KCPJS] | CONCENTRATIONS | | |
|----------------------------|-------------------|----------------|----------|-----------|
| | | 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 2: Regression results on grey cements

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