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APPLICATION NOTE

No. AN41301

Free Lime Determination in Clinker

ARL 9900 Series XRF Spectrometer with Compact Integrated XRD System

Key words
ARL 9900, cement, free lime, Integrated XRF-XRD, X-ray Fluorescence, X-ray Diffraction

Introduction

Calcination of cement raw materials in the kiln produces a material called clinker. Free lime (CaO) in clinkers has to be closely monitored to ensure the quality of cement. Excess free lime results in undesirable effects such as volume expansion, increased setting time or reduced strength. In addition, constant monitoring of free lime allows the operator to determine and maintain the optimum operating point of the kiln in order to obtain maximum reactivity and to reduce thermal consumption. With increased reactivity, grinding of the raw meal can also be reduced leading to further economies of energy.

The X-ray fluorescence technique (XRF) is used to perform chemical elemental analysis on cement making materials. From this analysis, concentrations for the major oxides are derived. Since mineralogical information is not available from XRF spectra (for instance XRF gives only the total Ca concentration in the sample including free CaO), wet chemical methods like titration or a separate X-ray diffractometry (XRD) equipment are normally required to determine the phase content in clinker or cement.

Thermo Fisher Scientific has introduced an innovative instrument capable of dealing with both techniques: the Thermo Scientific ARL 9900 Series with IntelliPower™. Inside the XRF spectrometer, a diffraction system can be integrated which is capable of performing qualitative scans and quantitative analysis as well. The highest repeatability of angular positioning is ensured through Thermo moiré fringe positioning mechanism.

The performance of this diffraction system has been improved by careful optimization of the crystal discriminator and the detector. A large gain on the sensitivity of the interesting phases has been obtained which results in much better performance in term of quantitative analysis than what is achieved with traditionnal diffractometers.

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Free lime analysis results

A series of six clinker standards were analyzed for free lime by wet chemistry. The powders were ground for 10 s with two 200 mg grinding pills. They were then pressed into pellets at 15t for 40s and measured on the ARL 9900.

Figure 1 shows the diffractogram recorded with the diffraction system on three different clinker pellets. The two peaks assigned to C_3S and CaO phases, are resolved and not interfered by any fluorescence from the sample. As can be seen from the peak, representing 0.5 % of free lime, the increased sensitivity of the diffraction system is more than adequate to monitor the free lime content even at low levels (0.1 % to 0.5 %).

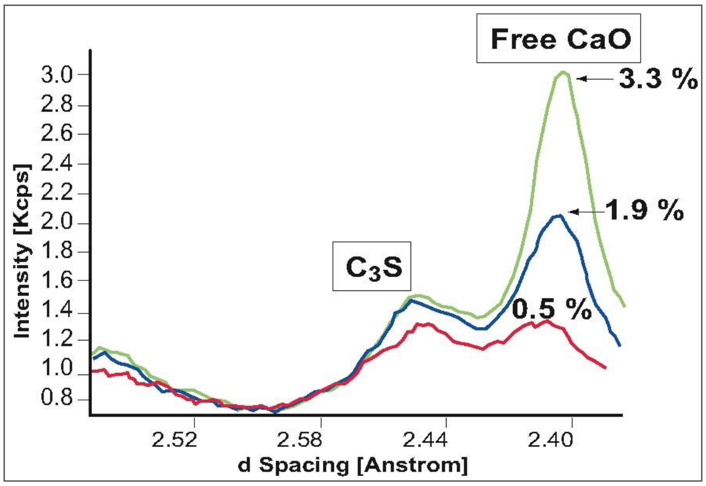

Figure 1: Diffraction pattern obtained with the ARL 9900 Series in the free lime region for clinker samples with varying CaO concentrations

A calibration program recorded the intensities of the characteristic diffraction peak for free lime (d=2.41Å) on the six clinker standards. The results are shown in Figure 2 along with the relevant parameters in Table 1. The innovative diffraction system produces a sensitivity of 600 cps/ % for free lime analysis. This is about 10 times higher than a conventional X-ray diffractometer. The standard error of estimate is an average of the differences between chemical and found concentrations. It is an estimation of the accuracy of analysis. The value obtained (0.08 %) is well within the capability of wet chemistry.

The short term stability was tested by measuring a clinker sample 11 times for 40 s on free lime with the integrated XRD system and 40 s on the fixed XRF channels. The results are summarized in Table 2 where XRF results on major oxide are also included for comparison. They show the fine repeatability of the system: ~1 % relative standard deviation. This is approximately 10 times better than what is achievable by wet chemistry.

Finally, a long term stability test was also performed over 50 hours. Excellent results were obtained with sigma values well within statistics (1.8 % free lime ± 0.02 %).

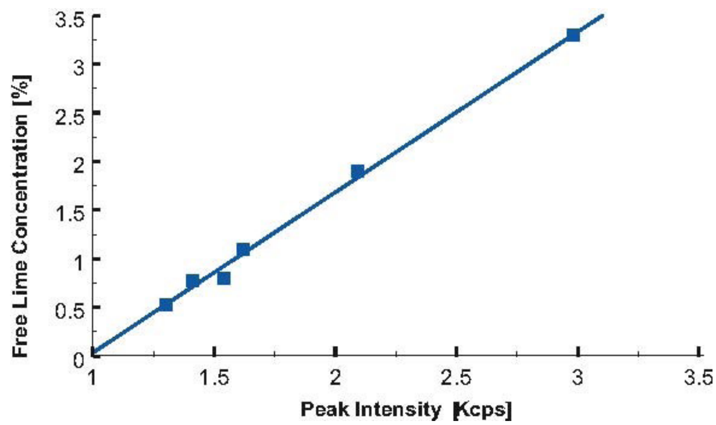

Figure 2: Calibration curve of free lime in clinker using the ARL 9900 Series.

Sample difference Absol. %	Concentration			
	Name	Kcps	Nom. %	Cal'd%
Clinker 1	1.54	0.80	0.93	0.13
Clinker 2	1.30	0.53	0.53	0.00
Clinker 3	2.98	3.30	3.32	0.02
Clinker 4	1.62	1.10	1.07	-0.03
Clinker 5	2.09	1.90	7.84	-0.06
Clinker 6	1.41	0.77	0.71	-0.06
Standard error of estimate			0.08 %	
BEC			1.636 %	
Q (sensitivity)			600 cps/ %	
Limit of Detection			156 ppm	

Table 1: Regression results on free lime

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Run	XRD	XRF							
	Free lime	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
1	0.67	65.54	21.42	5.59	3.97	1.55	0.68	0.58	1.01
2	0.68	65.52	21.41	5.59	3.96	1.55	0.68	0.58	1.00
3	0.67	65.52	21.41	5.59	3.96	1.55	0.68	0.58	1.00
4	0.66	65.50	21.40	5.58	3.96	1.55	0.68	0.58	1.00
5	0.67	65.50	21.39	5.58	3.96	1.55	0.68	0.58	1.00
6	0.66	65.52	21.41	5.58	3.96	1.55	0.68	0.58	1.01
7	0.66	65.52	21.41	5.59	3.96	1.54	0.68	0.58	1.00
8	0.67	65.51	21.41	5.58	3.96	1.55	0.68	0.58	1.00
9	0.67	65.51	21.41	5.59	3.96	1.55	0.68	0.58	1.00
10	0.65	65.50	21.39	5.59	3.96	1.55	0.68	0.58	1.00
Average	0.67	65.51	21.41	5.59	3.96	1.55	0.68	0.579	1.00
St Dev	0.007	0.014	0.011	0.009	0.004	0.003	0.001	0.002	0.001
RSD	1.04	0.02	0.05	0.16	0.10	0.18	0.09	0.27	0.08

Table 2: Typical reproducibility (10 runs) of free lime analysis in clinker. Included is also the usual XRF analysis. Total counting time: 80 s.

Conclusion

By using the diffraction system integrated into the ARL 9900, free lime in clinker can be quantified with high sensitivity, reliability and excellent stability.

Limestone additions to cement which are becoming increasingly important in Europe following recent regulations, can also be monitored using this integrated XRF-XRD instrument, as well as other clinker phases like C_3S, C_2S, C_3A or C_4AF and quartz content in raw meal.

The advantages of this combined system are obvious:

- XRF and XRD can be performed on the same sample and under identical conditions thus cutting down all extra costs for additional hardware and ensuring more reliable and stable total analysis.
- XRF performance is not affected by the addition of this diffraction system.
- Software and data treatment methods are common to XRF and XRD measurements.
- A rapid and flexible system can be configured based on fixed XRF channels for simultaneous analysis of all cement oxides, the diffraction system which has the capability of measuring free lime (CaO) and calcite ($CaCO_3$) phases, our Moiré fringe goniometer for a sequential XRF analysis on any of 86 elements of the periodic table and back-up of the fixed channels.

The combination of XRF and XRD in the same instrument can now 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 maintenance and running costs.

More than 500 ARL 9900 Series are in operation in cement plants around the world.

Find out more at **thermofisher.com/9900**

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