Free lime determination in clinker

ARL X900 Series XRF Spectrometer with compact integrated XRD system

Introduction

Calcination of cement raw materials in the kiln produces a material called clinker. Free lime (CaO) in clinkers must 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 for maximum reactivity and reduction of 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 calcium concentration in the sample including free CaO), wet chemical methods like titration or a separate X-ray diffractometer (XRD) are normally required to determine the free CaO phase content in clinker or cement. The X-ray diffraction technique permits determination of compounds (also called phases) in crystalline materials.

XRF and XRD in the same spectrometer

Thermo Fisher Scientific introduces an innovative instrument capable of dealing with both techniques: the Thermo Scientific™ ARL™ X900 Series Spectrometer. A diffraction system is integrated inside the XRF spectrometer and can perform qualitative scans and quantitative analysis as well. A single X-ray tube is used for both the XRF and XRD analysis.

The performance of the diffraction system has been improved by careful optimization of the crystal discriminator and the detector. The highest repeatability of angular positioning is ensured through the exclusive moiré fringe positioning mechanism.

A large gain on the sensitivity of the interesting phases results in better performance in terms of quantitative analysis compared to traditional diffractometers.

Figure 1. ARL X900 Series WDXRF Spectrometer with XRD capability.

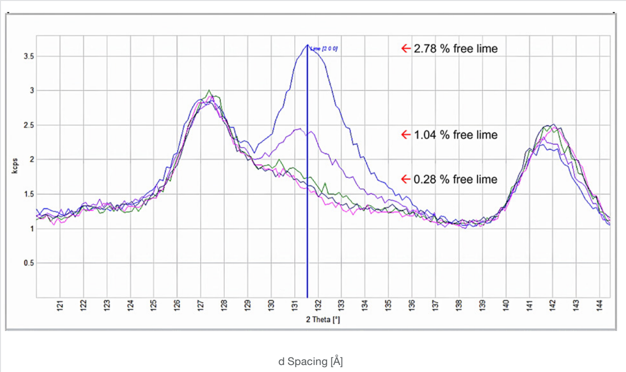

Figure 1. Diffraction pattern obtained with ARL X900 Series in the free lime region for three clinker samples with varying CaO concentrations.

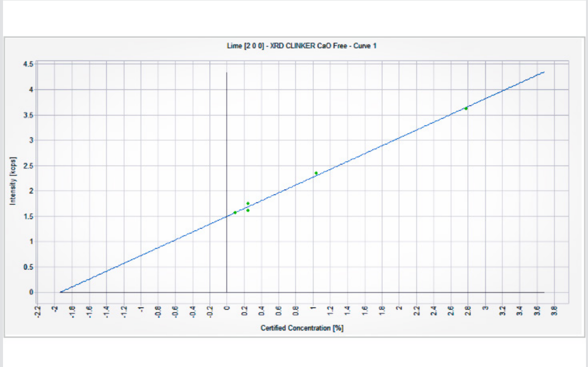

Figure 2. Calibration curve of free lime in clinker with ARL X900 Series.

Free lime analysis

Figure 1 shows the diffractogram recorded with the integrated diffraction system on five different clinker pellets. The two peaks assigned to C_3S and CaO phases, are resolved and not interfered by any fluorescence from the sample. The free lime content of these samples is shown. Usually, the free lime level in clinker is kept below 2% in routine production. But a higher free lime level can be obtained when clinker samples are collected either during a kiln shutdown or during kiln start-up.

Calibration curve and results

A series of five clinkers were analyzed for free lime. Either wet chemistry or Rietveld method on an independent diffractometer can be used. The clinker granules are first milled for 10s with 10% binder. They are then pressed into pellets at 10 t for 40s and measured on the compact XRD system of the ARL X900 spectrometer.

The calibration program records the intensities of the free lime diffraction peak (d=2.395 Å) on the five clinker standards, either at the peak position or through integration of the free lime peak. See Table 1. The calibration curve is obtained from the correlation of the concentration data and the measured intensities (Figure 2).

The innovative diffraction system produces a sensitivity of 774 cps/% for free lime analysis on the ARL X900 spectrometer. This is about ten times higher than a conventional X-ray diffractometer. The standard error of estimate (SEE) is an average of the differences between chemical and found concentrations. It is an estimation of the accuracy of analysis. The value obtained is well within the capability of wet chemistry.

Table 1. Regression results on free lime at 2500 W.

Concentration				
Sample name	**Intensity Kcps**	**Nominal %**	**Calcul'd %**	**Difference absol. %**
Clinker 1	3.626	2.78	2.75	-0.028
Clinker 2	2.351	1.04	1.10	0.064
Clinker 3	1.747	0.25	0.32	0.074
Clinker 4	1.612	0.24	0.15	-0.098
Clinker 5	1.567	0.10	0.09	-0.011
Standard error of estimate (SEE)			0.081%	
R^2			0.996	
Q (sensitivity)			774 cps/%	
Limit of detection (20s)			0.033% in 20s	

The short-term stability was tested by measuring a clinker sample for 10 successive analyses. Counting time was 30 seconds on free lime with the integrated XRD system except for Fe, K, Mg, and Na which were measured in 10 seconds. The results are summarized in Table 2. The fine repeatability of the spectrometer for free lime and the other elements / oxides is shown. Free lime precision is about 10 times better compared to wet chemistry.

With a limit of detection of 0.033% in 20 s counting time, the integrated diffraction system is more than adequate to monitor the free lime content in clinker even at levels below 1% as shown in Table 3.

Table 2. Typical repeatability (10 runs) of free lime analysis in clinker at 2500W. Free lime and usual XRF data are included. Total counting time: 190 seconds per run with goniometer and 50 seconds in case fixed XRF channels are fitted for all elements/oxides.

Power level 2500W	XRD	XRF									
	XRD free lime %	CaO %	SiO2 %	Al2O3 %	Fe2O3 %	K2O %	MgO %	Na2O %	SO3 %	P2O5 %	Cl ppm
Goniometer	30s	20s	20s	20s	10s	10s	10s	10s	20s	20s	20s
1	1.54	65.33	22.49	3.942	3.655	0.899	3.389	0.129	0.113	0.032	79
2	1.50	65.35	22.48	3.941	3.645	0.891	3.378	0.123	0.112	0.031	79
3	1.53	65.32	22.46	3.940	3.651	0.895	3.385	0.124	0.109	0.031	80
4	1.51	65.34	22.48	3.941	3.643	0.896	3.387	0.128	0.111	0.031	81
5	1.52	65.33	22.49	3.948	3.645	0.897	3.373	0.126	0.116	0.032	80
6	1.55	65.31	22.48	3.950	3.647	0.894	3.381	0.125	0.113	0.031	79
7	1.52	65.32	22.49	3.943	3.655	0.899	3.377	0.129	0.113	0.031	80
8	1.54	65.34	22.50	3.941	3.645	0.897	3.388	0.124	0.113	0.030	81
9	1.50	65.32	22.49	3.943	3.642	0.891	3.376	0.126	0.111	0.031	85
10	1.51	65.30	22.49	3.949	3.638	0.895	3.384	0.121	0.116	0.031	80
Average std dev.	**1.52 0.018**	**65.33 0.015**	**22.49 0.011**	**3.944 0.004**	**3.647 0.006**	**0.895 0.003**	**3.382 0.006**	**0.126 0.003**	**0.113 0.002**	**0.031 0.0004**	**80.5 1.7**

Table 3. Comparison of repeatability (6 runs) for free lime analysis in clinker at 2500W. At just 60s counting time the precision is excellent, but it is also quite good at 20 s counting time.

Clinker A	Free CaO	Free CaO
	60s counting	20s counting
Run 1	0.811	0.797
Run 2	0.795	0.814
Run 3	0.805	0.802
Run 4	0.805	0.815
Run 5	0.805	0.791
Run 6	0.794	0.788
Average	**0.802**	**0.801**
Std deviation	**0.007**	**0.012**

Conclusion

By using the diffraction system integrated into the ARL X900 Spectrometer, free lime in clinker can be quantified with high sensitivity, reliability, and excellent stability.

Limestone additions to cement 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 the integrated diffraction system and our innovative Moiré fringe XRF goniometer for sequential XRF analysis on any of 86 elements of the periodic table and the integrated diffraction system. A few fixed XRF channels can be added for speed through simultaneous analysis of any cement oxide.

The ARL X900 Series is the successor of the famous Thermo Scientific™ ARL™ 9900 Series of which more than 500 units are in operation in cement plants around the world.

Learn more at **thermofisher.com/X900**

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