Application note

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Applications in cement industry

ARL X900 Simultaneous/Sequential X-Ray Fluorescence Spectrometer

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Figure 1. ARL X900 WDXRF Spectrometer with 20-position sample loader.

Introduction

Wavelength dispersive X-ray fluorescence (WDXRF) allows measurement of up to 84 periodic table elements in samples of various forms and nature: solids or liquids, conductive or non-conductive. Advantages of XRF over other techniques are speed of analysis, easy sample preparation, consistent stability, precision, and wide dynamic range (from ppm levels to 100 %).

X-ray fluorescence is the technique of choice for elemental analysis in the cement industry as it allows the analysis of major and minor oxides in the raw materials, clinker, and cement.

Since mineralogical information is not available from XRF spectra (for instance XRF gives only the total calcium concentration in the sample), wet chemical methods like titration or X-ray diffractometry (XRD) equipment are normally required to determine the phase content in clinker or cement.

Instrumentation

The Thermo Scientific™ ARL™ X900 Spectrometer is a WDXRF instrument designed for ease-of-use with minimal operation and maintenance costs. This spectrometer can be fitted with a universal goniometer covering elements from fluorine (^{9}F) to americium (^{95}Am)* and several fixed monochromator channels to enable faster analysis when required. A rhodium anode X-ray tube is used, and the geometry of the instrument is optimized to provide the highest sensitivity.

*Upon special request, the goniometer can accommodate elements ranging from boron to americium.

Three power versions are available. The 1500 W or 2500 W models operate without external water cooling. The highest power 4200 W version requires external water cooling, either through tap water or a water chiller. Compressed air is never needed and the consumption of P10 detector gas is minimized to one large bottle of 50 liters every 30 months.

At all power levels, the goniometer shows high precision and stability and has excellent performance for all element/oxides including sodium (^{11}Na), magnesium (^{12}Mg) and even fluorine (^{9}F).

In addition, an innovative X-ray diffraction (XRD) system can be integrated in the large vacuum tank. This mechanism permits analysis of several phases that are useful for monitoring various processes during cement manufacture.

Ease-of-operation is obtained through the Thermo Scientific™ OXSAS™ Analysis Software that allows connection to LIMS and automation software when required.

Applications

The ARL X900 spectrometer is modular and can offer both XRF and XRD techniques in the same instrument. It can cover several applications in the cement industry.

The first requirement in any cement industry process and quality control laboratory is the elemental analysis for the determination of CaO, SiO_2, Al_2O_3, Fe_2O_3, MgO, SO_3, K_2O, Na_2O, P_2O_5, TiO_2, Cl, etc. in raw meal, clinker and cement.

The ARL X900 spectrometer can be factory calibrated to provide a turnkey solution for the new user. As example table 1 lists the ranges that are covered with the factory calibration for clinker and cement with a sample preparation as pressed pellets.

Both the goniometer and fixed monochromator channels can be used for the analysis of these various elements/oxides. The goniometer measures the elements one after the other in a sequential mode, usually for 10 to 20 seconds each, while the fixed channels measure simultaneously. The number of fixed channels depends on the required speed of analysis and the desired sample throughput.

ARL X900 Series	
Element	**Typical range [%] for Portland cements**
CaO	57.6 - 67.8 %
SiO_2	19.3 – 22.4 %
Fe_2O_3	0.15 – 3.7 %
MgO	0.8 – 3.6 %
Al_2O_3	3.8 - 7 %
K_2O	0.025 - 1.2 %
Cl	0.0019 - 0.018 %
Na_2O	0.02 – 0.29 %
SO_3	2.1 - 4.6 %
P_2O_5	0.022 – 0.24 %

Table 1. Concentration ranges for cement calibration.

Fluorine content

The addition of CaF_2 in cement helps decrease the fusion temperature in the kiln and therefore saves energy. Control of the amount of CaF_2 can be done by measuring the fluorine content by XRF. It is done either in the raw meal or in the clinker. But the fluorine XRF signal is strongly absorbed by carbon, hence the performance of this analysis is rather poor in raw meal due to the large presence of CO_2, while it works better in clinker due to the absence of carbon.

Sulfur/sulfate determination

When metallurgical slags (GBFS) are added to cement, it is possible to determine the actual slag content by X-ray fluorescence. The sulfur vs. sulfate determination is done on the sulfur K beta satellite peak that is a signature for clinker. The more slag is present, the lower the satellite peak will be. The goniometer of ARL X900 spectrometer is usually selected for this measurement, but a fixed channel dedicated for the analysis of the sulfur satellite peak can also be configured.

Variety of raw materials and products

When using a sample preparation as fusion beads many different materials can be measured with the same calibration. For example, limestone, marl, iron ore, slags, clinker, cement and raw meal are all included in the same calibration. The ARL X900 spectrometer can be factory calibrated with this “General Oxide” calibration that provides a turnkey solution for analysis of 12 elements/oxides.

Use of the integrated X-ray diffraction system

The integrated X-ray diffraction system in ARL X900 spectrometer permits fulfilling several applications in the cement industry as shown below.

Quartz in raw meal

The presence of quartz (α-SiO_2) particles larger than 45 microns in the raw materials can be very detrimental to the final compressive strength of cement. Quartz content can be determined by the integrated XRD system of ARL X900 spectrometer.

Hot meal - degree of decarbonation

In the cyclones of the pre-heating tower, the raw meal temperature reaches 500 °C at the top of the tower and 900 °C at the kiln inlet. This temperature increase means that calcium carbonate will be calcined as follows: $CaCO_3 \rightarrow CaO + CO_2$.

Using its integrated X-ray diffraction, the ARL X900 spectrometer can help control the formation of CaO in the hot meal while $CaCO_3$ disappears.

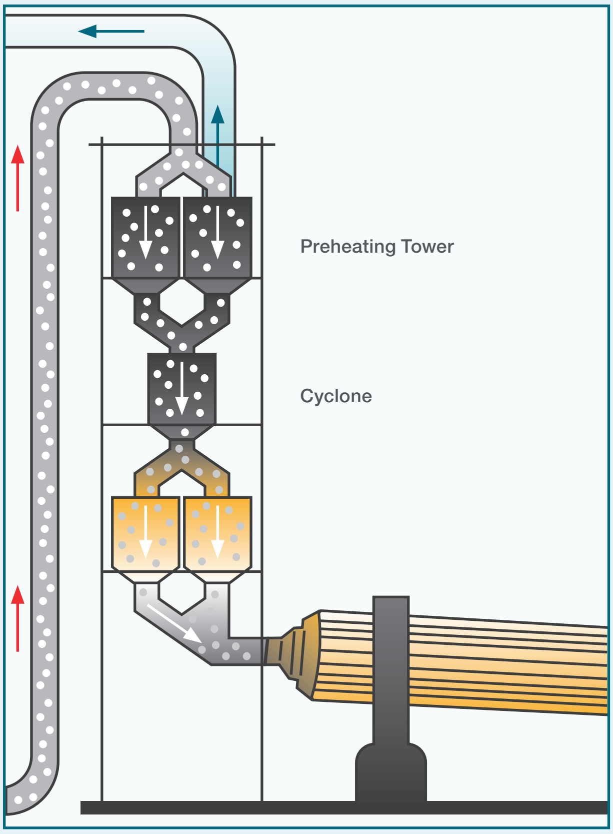

Figure 2. Pre-heating tower in a cement plant.

Free lime in clinker (CaO)

During hydration, free lime reacts with water and swells ($CaO + H_2O \rightarrow Ca(OH)_2$), therefore free lime must be kept below 2 % in the final cement to avoid any troubles.

In the kiln at temperatures higher than 1350°C, free lime reacts with belite ($C_2S = 2CaO.SiO_2$) to produce alite ($C_3S = 3CaO.SiO_2$). Alite brings higher compressive strength to clinker and is therefore mostly valuable. Clearly when more free lime is consumed during this reaction, then more C_3S is formed. This results in a high resistance cement, but at the same time more energy has been used to keep a high temperature in the kiln. A balance between higher C_3S formation and energy consumption must be found. Controlling the free lime level by X-ray diffraction helps to find this balance.

Clinker phases

The acronyms of the major clinker phases are C_3S, C_2S, C_3A ($3CaO.Al_2O_3$), C_4AF ($4CaO.Al_2O_3.Fe_2O_3$). As explained above, a part of C_2S is consumed in the kiln to form C_3S. The early strength of cement is provided by the C_3S phase, but also by C_3A as both phases react quickly when hydrated. This is why it is useful to control the presence of these phases in clinker. For many decades, these phases have been determined through the Bogue equations, but these equations provide approximative values that can be seriously misleading. X-ray diffraction is much more reliable and the integrated diffraction system of ARL X900 spectrometer can do their analysis in a couple of minutes.

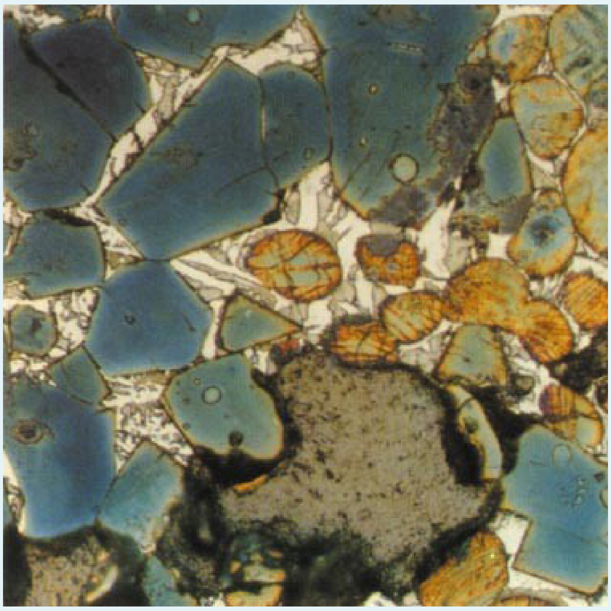

Figure 3. Microscopy of a clinker – C_3S in blue, C_2S in grey, C_4AF in braun and C_3A in white.

Clinker content in cement

Cement is composed of clinker, gypsum and other additives like limestone, metallurgical slags, pozzolan and fly ash. Clinker is the most expensive part of cement and its content in cement can be determined directly using the integrated XRD system of ARL X900 spectrometer.

Limestone additions in cement

Limestone ($CaCO_3$) is often added to cement which results in a lower compressive strength, but better malleability. The percentage addition of $CaCO_3$ can be controlled by the integrated XRD of ARL X900 spectrometer.

Pozzolan additions

Pozzolan or materials with pozzolanic properties are often used as additives to cement in order to get a high compressive strength after a several weeks of curing. If an XRD signature exists for the additive, its percentage can be controlled by the integrated XRD of ARL X900 spectrometer.

Free lime and amorphous content in GBFS

Granulated blast furnace slags (GBFS) are added to cement in order to get a high compressive strength after a few weeks of curing. For best results, it is important that the slags are as much amorphous as possible and contain low levels of free lime (< 5%). Both the free lime level and the amorphous content of slags can be controlled by the integrated XRD of ARL X900 spectrometer.

Amorphous content in cement

An amorphous material does not produce X-ray diffraction peaks. The amorphous content in cement can be controlled by measuring the spectral background on the integrated diffraction system.

Conclusion

The ARL X900 WDXRF Spectrometer permits successful analysis of a dozen oxides/elements in cement and clinker in less than two minutes. Pressed pellet sample preparation is fast and simple and allows lower limits of detection and good precision. Preparation through fusion with lithium borate flux is used when several diverse minerals should be measured with the same calibration with the best possible accuracy.

The goniometer can measure all required elements. If better precision is required for any element, the counting time for that element can be increased. In view of the excellent standard deviations obtained, the counting time for some elements can be decreased, e.g. to less than 10s for K_2O, P_2O_5, TiO_2, and MnO thus reducing the total counting time.

One or several fixed monochromator channels can be added to the ARL X900 Spectrometer and measure at the same time as the goniometer. In that case, the total counting time is further reduced.

An innovative X-ray diffraction system can also be integrated with the spectrometer that permits the analysis of several useful phases in slags, clinker and cement.

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