

# Integrated X-ray analysis

by Ravi Yellepeddi,  
Raphael Yerly and  
Didier Bonvin,  
Thermo Fisher Scientific,  
Switzerland

*There is increasing demand for comprehensive chemical and phase analysis in the cement industry. While traditional elemental or oxide analysis is well established, the use of X-ray diffraction (XRD) as a routine technique is gaining popularity among cement chemists. Reliable quantitative phase analysis alongside total oxide analysis provides valuable information in the cement making process. Indeed, integrated analysis combining X-ray fluorescence (XRF) and XRD for chemical and mineralogical characterisation is an efficient method in the management of raw materials, kiln feed and clinker production. This total solution is vital for the quality control of final cement products with a variety of additives or admixtures such as slags, fly ash, limestone and others.*

The increasing use of alternate fuels in clinker manufacturing has necessitated closer monitoring of clinker phases and possible variations of the quality of final product. It is becoming more common to use XRD in conjunction with XRF to detect changes in the clinker quality and to help to understand the effects of the use of alternate fuels as distinguished from the variations in the kiln feed itself. There are obvious economic and ecological interests with the use of this process as well as ensuring the physico-chemical properties of the final cement product.

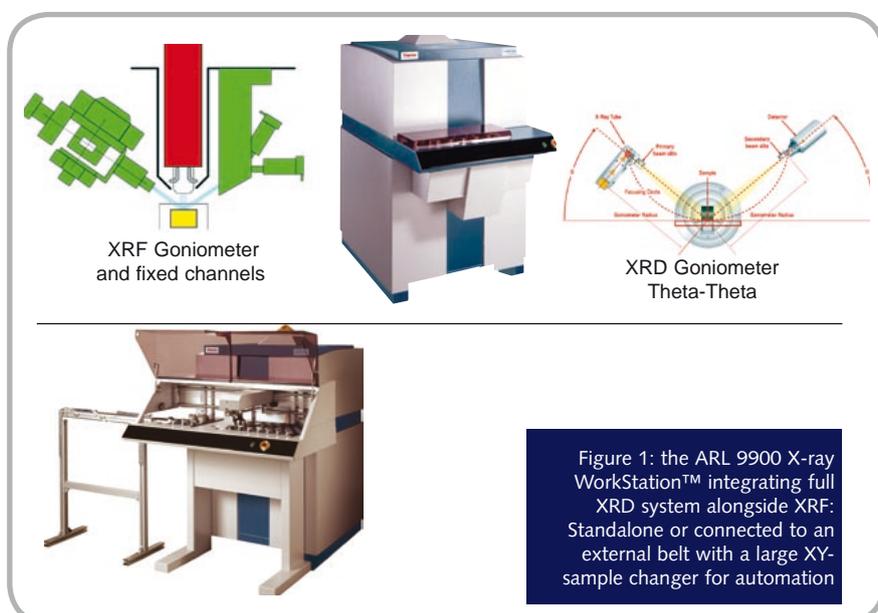
The use of XRD in cement process control has increased with the development of integrated X-ray instruments which are designed for reliable and fast quantitative analysis of

specific phases of interest such as free lime in clinkers. The use of total cement analysers, integrating both chemical and priority phase analysis, has also significantly increased in the last decade resulting in cement laboratories not only gaining confidence in exploiting the benefits of XRD but also enabling the scope of phase analysis to be optimised. In addition to the significant innovations in integrated XRF-XRD instrumentation, robust and sophisticated quantitative phase analysis programs based on Rietveld method also help in fostering the extensive use of X-ray diffraction in a process control environment. This article discusses the latest developments in X-ray instrumentation and analytical techniques in response to the cement industry's requirements.

## Breakthrough technology

One of the key requirements for the process and quality control environment is a reliable, integrated on-line system combining XRF and XRD capabilities. This ensures high sensitivity, stability and precision. The first generation of integrated XRF-XRD instrumentation was developed more than 10 years ago and used a single Rhodium target X-ray tube to excite the sample for XRF and at the same time, for the diffraction of different minerals present in the same sample. This system was optimised for the highest sensitivity under vacuum for critical phases such as free lime and clinker phases. In addition to these important phases for routine process control, it became clear that information about phases such as periclase, quartz, gypsum in cement and additives of crystalline or non-crystalline nature is very useful to control the complete workflow. In order to achieve a more extensive phase analysis, the integration of a full XRD and XRF instrument was developed. This breakthrough technology is based on geometry with the sample analysis surface positioned upwards with both XRF and XRD systems above the sample. This orthogonal disposition is the most preferred geometry ensuring a high degree of liberty to integrate several analytical devices together, all under vacuum and in a thermally stabilised environment. These conditions are important in order to achieve the precision, long-term stability and sensitivity for fast analysis.

Data acquisition for uncompromising



**Table 1: the repeatability (precision) data of various oxides using XRF Goniometer (SmartGonio™) at 2500W. The total analysis time is 80 seconds**

Run	Al <sub>2</sub> O <sub>3</sub>	CaO	Cl	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Mn <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	SiO <sub>2</sub>	SrO	TiO <sub>2</sub>
1	5.281	63.81	0.0199	2.895	0.933	2.775	0.085	0.283	0.300	3.430	20.51	0.064	0.233
2	5.253	63.81	0.0197	2.880	0.931	2.790	0.083	0.285	0.296	3.412	20.48	0.063	0.233
3	5.273	63.84	0.0204	2.889	0.929	2.774	0.082	0.287	0.303	3.425	20.54	0.065	0.235
4	5.230	63.78	0.0200	2.883	0.931	2.745	0.083	0.290	0.300	3.419	20.47	0.063	0.232
5	5.229	63.79	0.0201	2.897	0.936	2.771	0.083	0.288	0.296	3.420	20.53	0.064	0.241
6	5.239	63.85	0.0200	2.877	0.935	2.785	0.084	0.296	0.297	3.428	20.53	0.064	0.237
7	5.249	63.82	0.0206	2.892	0.932	2.768	0.083	0.288	0.304	3.432	20.48	0.063	0.230
8	5.255	63.81	0.0195	2.885	0.939	2.770	0.084	0.283	0.301	3.431	20.48	0.063	0.240
9	5.263	63.79	0.0199	2.878	0.930	2.764	0.086	0.296	0.295	3.438	20.50	0.063	0.234
10	5.258	63.83	0.0198	2.879	0.932	2.767	0.084	0.281	0.300	3.436	20.52	0.064	0.233
11	5.256	63.85	0.0204	2.887	0.935	2.773	0.082	0.291	0.298	3.437	20.53	0.064	0.237
Average	5.253	63.814	0.020	2.886	0.933	2.771	0.084	0.288	0.299	3.428	20.506	0.064	0.235
Sigma	0.016	0.023	0.0003	0.007	0.003	0.012	0.0012	0.005	0.003	0.008	0.026	0.0006	0.003
RSD (%)	0.31	0.04	1.56	0.24	0.32	0.42	1.46	1.77	0.97	0.24	0.13	0.97	1.44

XRF analysis, together with full range XRD scan for quantitative phase analysis, is preferably accomplished using a single interface and a seamless data processing tool. Since XRF requires a vacuum environment (for measurements down to sodium and even to fluorine in some cases), the ability to use the same environment to perform full range XRD measurements is particularly beneficial. Both XRF and XRD measurements are taken under a controlled atmosphere with the same sample positioning. The XRF analysis can be carried out using a goniometer in a sequential manner or it can also be performed simultaneously using a series of XRF monochromators. The XRD scan is obtained using an independent theta-theta (Bragg-Brentano) goniometer within the same spectrometer tank. Both the XRD tube and the XRD detector have been designed and optimised to ensure maximum sensitivity either to detect low concentration phases or to achieve fast XRD analysis for majority of the phases. XRF and XRD measurements are taken without any mutual interference or cross-talk. Additionally, the same software interface manages the priority of events between XRF and XRD in order to minimise the overall analysis time. The user can also select the report of chemical analysis (XRF) first followed by complete phase analysis (XRD) or

Figure 2: overview of XRD scans on a series of cement samples obtained using the Thermo Scientific ARL 9900 X-ray WorkStation

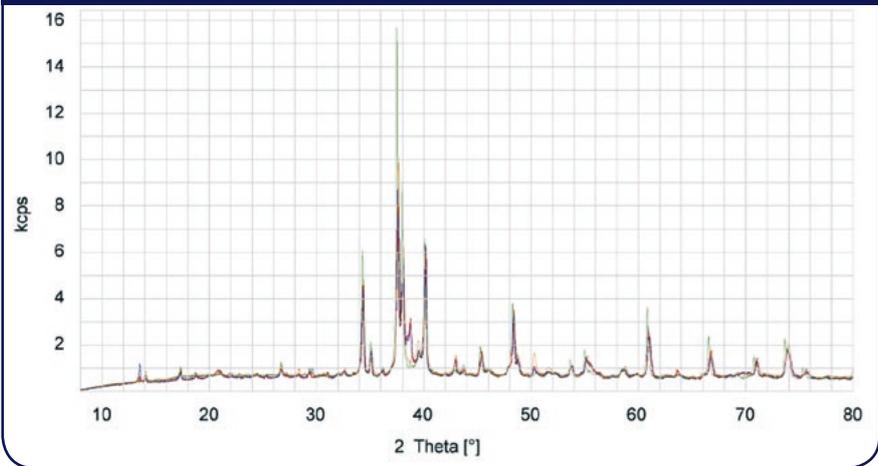
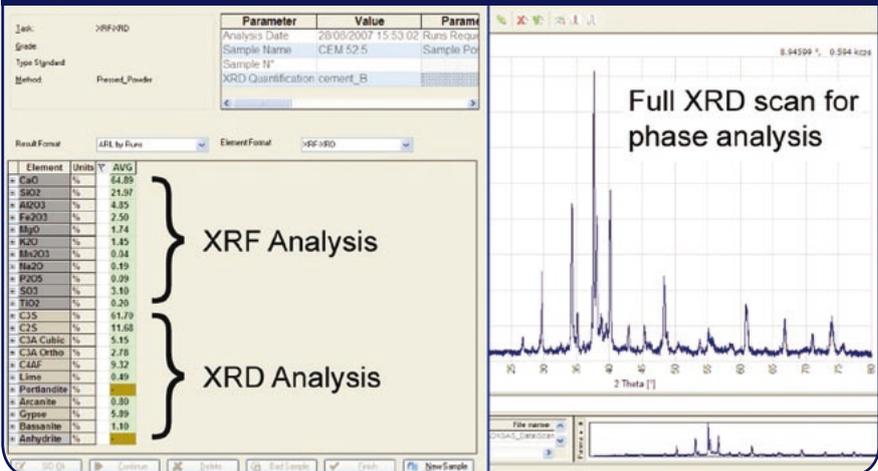


Figure 3: quantitative chemical and phase analysis on a cement sample using the ARL 9900 X-ray WorkStation. The right hand side insert shows the X-ray diffraction scan used for the phase quantification. A single report is issued at the end of the total analysis, providing a possible synergy or data correlation between XRF and XRD



vice versa. While the XRF analysis is reported using the calibration programs for each matrix type as usual, the XRD scan is automatically processed using the integrated phase quantification program. A pre-defined control file is used for the automatic phase quantification. Such an approach assumes that the initial parameters have been studied and set up for routine phase analysis in a given process control environment. Alternatively, the XRD raw data can also be exported to an external Rietveld program for processing and detailed investigations.

Figure 1 shows the Thermo Scientific ARL 9900 X-ray WorkStation™ which integrates full range XRD capability inside an XRF spectrometer under vacuum. While the XRD measurements are usually taken with copper or cobalt anode X-ray tubes around 2kW power, the XRF measurements are accomplished using an Rh target tube. The latter can be operated at different power conditions: 1200W and 2500W requiring no external water chiller, or 3600W and 4200W with an external chiller for ultimate performance. The most practical and uncompromising measurements are recorded at 2500W for XRF in line with the XRD power thus eliminating the need for an external water cooler for both techniques. In addition, the sample introduction is unique to both the techniques.

The complete analysis of XRF and XRD is reported together, enabling cross-checks between chemistry and mineralogy. The phase compositions can be converted back to the equivalent total oxide values by reverse Bogue if needed. Inter-phase or inter-element corrections can also be performed to understand various correlations.

The scope of analysis enables the user to exploit or explore the total characterisation of the materials involved. With a new generation of XRD detector and optimisation of XRF channels within the same framework, fast, reliable and accurate measurements can be achieved. The ARL 9900 X-ray WorkStation is designed to be integrated into an automated or semi-automated laboratory involving either a robotic system or a large XY-sample changer driven by an engineering package.

Automation capabilities range from simple link to automatic sample preparation machines with an interface from a central control system to the robot-based Thermo Scientific ARL SMS-3000 for a completely autonomous X-ray analysis laboratory.

## Results and discussion

A series of clinker and cement samples were measured using both XRF and full XRD on the same sample and with one analytical program. Using optimum X-ray power and performance criteria, XRF measurements were taken at 2500W while the XRD measurements are performed under the standard conditions with a copper anode tube or cobalt anode tube within the same instrument.

Figure 2 shows the full range X-ray diffraction patterns for a series of cement samples with varying concentrations of alite ( $C_3S$ ), belite ( $C_2S$ ), aluminite ( $C_3A$ ) in both orthorhombic and cubic forms, ferrite ( $C_4AF$ ) in addition to free lime, gypsum, periclase, quartz and other phases. Following the acquisition of this full pattern XRD scan, (required for Rietveld or similar phase quantification programs) the data processing is

Figure 4: XRD scans zoomed around periclase (MgO) in a series of cement samples

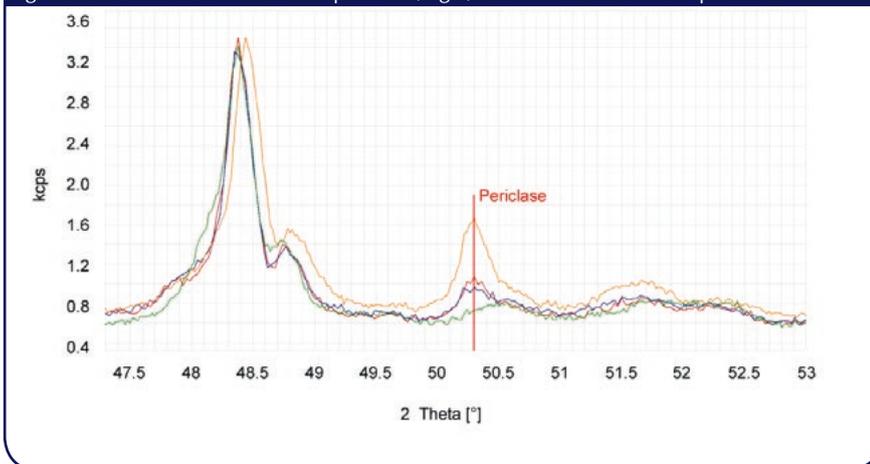
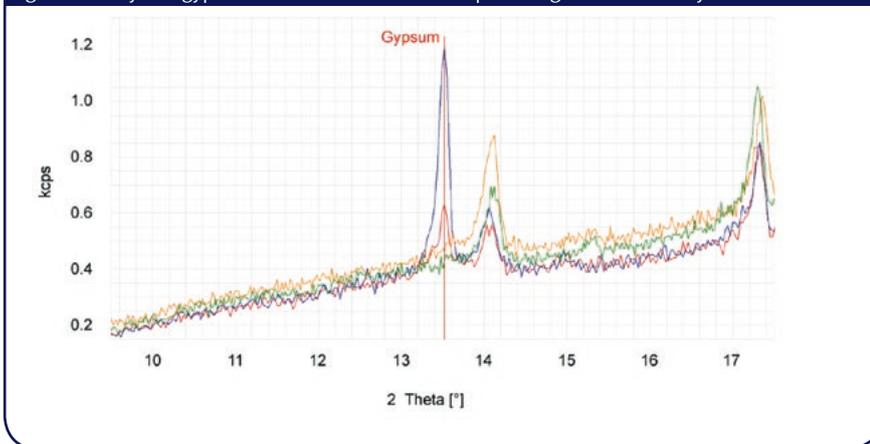


Figure 5: analysis of gypsum in a series of cement samples using ARL 9900 X-ray WorkStation



accomplished using a pre-set list of phases for direct and automatic quantification or by using more interactive methods for investigations. In both cases, the XRD results are adjoined to the XRF results obtained and a complete analytical report is produced to the user.

Figure 3 is an example of a report showing complete XRF analysis of all oxides alongside the full list of phase analysis by XRD. The right hand side of the figure shows the XRD scan retrieved immediately after the measurement for data processing. Both qualitative and quantitative information is available at any time for further research of the various phases on interest.

If more detailed or specific investigation is required, users can revert to the full XRD scan and refine or adjust the parameters for a more consistent analysis. It is also possible to focus on minor but important phases for a given process. Two examples are shown in Figures 4 and 5: XRD scans zoomed around periclase and gypsum in a series of cement samples.

Long-term stability and reproducibility

of XRF and XRD are very critical for a process control laboratory and utmost

importance is attached to the parameters which can influence them. As a proof of performance, a series of cement samples were run using a periodic sample-in sample-out loop and XRF results for total oxides and XRD results for phases were monitored continuously. This was carried out to simulate a traditional production control environment and the results are shown in Figure 6.

## Conclusions

Over the last decade, there has been a growing demand for a complete range of XRF-XRD instrumentation, with an increasing need for full phase identification, in addition to elemental analysis. The 9900 X-ray WorkStation integrates a full range XRD inside an XRF instrument, providing the most comprehensive analytical capability for uncompromising chemical and full phase analysis from raw materials to the final product.

This solution overcomes the many key issues including quality regulations, environmental concerns, energy efficiency and related cost of production. With increased confidence in implementing XRD in routine process control, the cement industry can take full advantage of full XRD capability along with uncompromising XRF analysis.

Figure 6: examples of stability tests in which both XRF channels and XRD results are monitored over several weeks without any drift correction

