# Analytical Solutions

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## Introduction

X-ray techniques are well established as part of an analysis system in the cement industry, but state of the art technology offers new, cost effective and intelligent solutions. A variety of systems are available starting from bench top Energy Dispersive X-ray Fluorescence (EDXRF) instruments to more sophisticated and integrated X-ray Fluorescence - X-ray Diffraction (XRF-XRD) platforms.

New entry level Wavelength Dispersive X-ray Fluorescence (WDXRF) instruments using low X-ray power and compact Goniometers have been developed. These can provide basic oxide analysis in a precise and highly reliable manner. This is the most cost effective solution for a small cement plant or a grinding station, or for a backup instrument in a large cement plant.

For medium sized to high capacity production units, XRF systems with integrated XRD present the most advantageous solution in terms of chemical and phase analysis for online control.

Ultimately, a high power stand-alone sequential XRF instrument in conjunction with a high performance stand-alone XRD instrument for rapid data acquisition and processing provide the best analytical capability in a central laboratory for method development and advanced applications.

Furthermore, a benchtop EDXRF instrument is best suited for the analysis of non-routine samples such as products for incineration in the kiln, air filters for

*Figure 1. ARL OPTIM'X - entry level WDXRF.*


*Figure 2. ARL 9900 XRF-XRD integrated spectrometer capable of operating at 1200 W without external water cooling or up to 4.2 kW for the most demanding analysis.*

monitoring the emission of toxic elements, etc.

This article will review the various X-ray solutions as a function of analytical needs in each of these cases and will propose intelligent solutions in the context of real industrial environment.

## Case 1

The analytical requirements in a small cement plant or in a grinding station can be summarised as below:

- Limited to the essential oxides for the process control and/or quality control in the final product.
- Lower sample throughput.
- Much lower capital investment.
- Easy to use, easy to maintain instruments with significantly lower running costs.

Some of the smaller plants may still depend on wet chemical methods for the analysis of the four major oxides. Others may have compromised on the analysis of some elements such as sodium and magnesium with low cost XRF instruments, either with poor sensitivity or poor precision. The availability of cost effective WDXRF instruments such as ARL OPTIM'X has made it possible to achieve reliable and repeatable analysis of all the oxides down to Na.

Equipped with a series of monochromators for simultaneous analysis or with SmartGonio™ technology for a more flexible solution, this instrument can provide analysis, for example, of 11 oxides with the required precision within 200 seconds. Since the instrument does not require internal or external water cooling and operates at low power, the running and maintenance costs are kept minimal yielding a low cost per analysis index. ARL OPTIM'X can also be integrated into the process stream using a simple OEM automation mode.

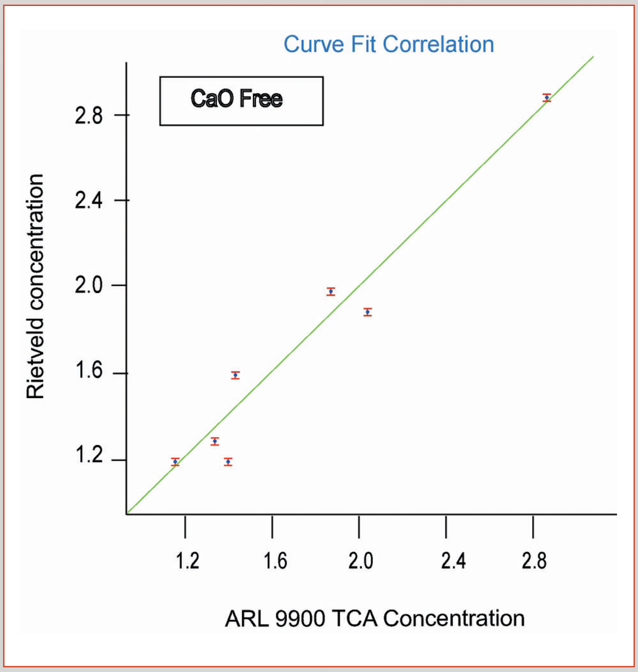


*Figure 3. Quantitative analysis of free lime using the ARL 9900 Total Cement Analyser. Accuracy: 0.15%.*

## Case 2

The analytical requirements of a medium to large size cement plant can be summarised as follows:

- Routine quantitative analysis of all the oxides with a high degree of accuracy and reliability.
- Dedicated calibration programs for each major matrix from raw materials to the final product quality.
- Reliable online analysis of free lime in clinkers as one of the most important kiln control parameters.
- Continuous quantitative monitoring of clinker phases as quality indicators.
- Quantification of additives such as limestone and slags in cement.
- Occasional non-routine analysis.

Any conventional medium to high power XRF spectrometer can easily meet the analytical performance and throughput requirements in such plants. Nonetheless, reliable, online monitoring of free lime and clinker phases simultaneously on the same sample provides added value for the process control. Indeed, ARL 9900 with its patented XRF-XRD technology which truly integrates the chemical and phase analysis (for example on clinker samples) offers an intelligent solution for routine process control.

**Table 1. Analytical performance obtained in 200 seconds with an entry level WDXRF instrument in terms of precision (repeatability) compared with typical requirements.**

| Element/Oxide | Concentration level | Required S.D. | S.D. obtained |
|---|---|---|---|
| CaO | 63.8 | 0.03 - 0.035 | 0.033 |
| $SiO_2$ | 20.3 | 0.02 | 0.02 |
| $Al_2O_3$ | 5.2 | 0.02 | 0.016 |
| $Fe_2O_3$ | 2.8 | 0.01 - 0.02 | 0.014 |
| MgO | 1.7 | 0.02 | 0.024 |
| $Na_2O$ | 0.2 | 0.015 | 0.007 |
| $K_2O$ | 0.9 | 0.02 | 0.01 |
| $SO_3$ | 3.2 | 0.01 - 0.015 | 0.013 |
| $P_2O_5$ | 0.2 | 0.01 - 0.015 | 0.013 |
| $TiO_2$ | 0.2 | 0.015 | 0.005 |
| $Mn_2O_3$ | 0.1 | 0.015 | 0.003 |

Table 2 shows the excellent repeatability obtained with ARL 9900 OASIS version at 1200 W power using a standard cement pellet.

There is increasing interest in cement production plants in extending the applicability of the XRD technique beyond the well established free lime analysis. Indeed, following the successful implementation and widespread use of integrated XRF-XRD systems (for the analysis of free lime in clinkers, limestone additions in cement, etc.) in the past 10 years, the XRD technique has become more familiar for routine usage by non-experts and without the need for multiple instrumentation.

It is clear that XRD as a technique can offer more to the cement chemist by characterising the raw materials for their mineralogy, quantifying the various clinker phases and controlling the additives or fillers in the final product. The choice is certainly there to explore: while an integrated XRF-XRD instrument offers an easy to implement, process dedicated solution for online quantification, a standalone XRD instrument provides an investigative and flexible tool for a central laboratory where the adequate know-how is also available. Clearly, several factors must be taken into account before choosing the most appropriate solution.

In the case of process/quality control, quantitative analysis of free lime and the clinker phases using the integrated XRD system is just as easy, reliable and repeatable as XRF analysis on the same sample under vacuum. Calibration programmes can be set up for free lime and the clinker phases using a series of clinker samples from the production site representing the true kiln conditions and process variations. The free lime concentrations are generally obtained using the wet chemical analysis without any difficulty. Figure 3 shows the excellent correlation obtained between the XRD intensities and the wet chemical values. This is probably the most practical method for a critical kiln control parameter such as free lime.

On the other hand, quantification of clinker phases ($C_3S$, $C_2S$, $C_3A$ and $C_4AF$) can be accomplished by using data from optical microscopy or an independent Rietveld based quantitative phase analysis programme. This latter method can be used to produce a

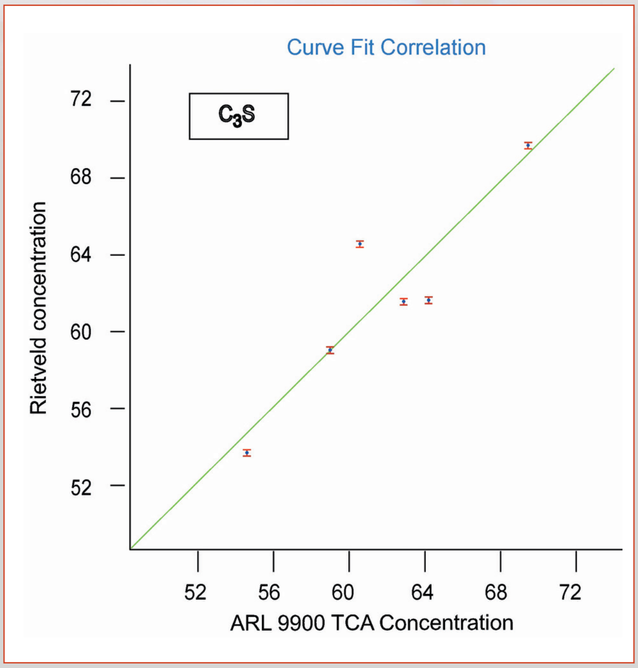


*Figure 4. Calibration curve for $C_3S$ phase using the integrated XRD system of the ARL 9900 and ClinkerQuant™ based on the Rietveld method as reference.*

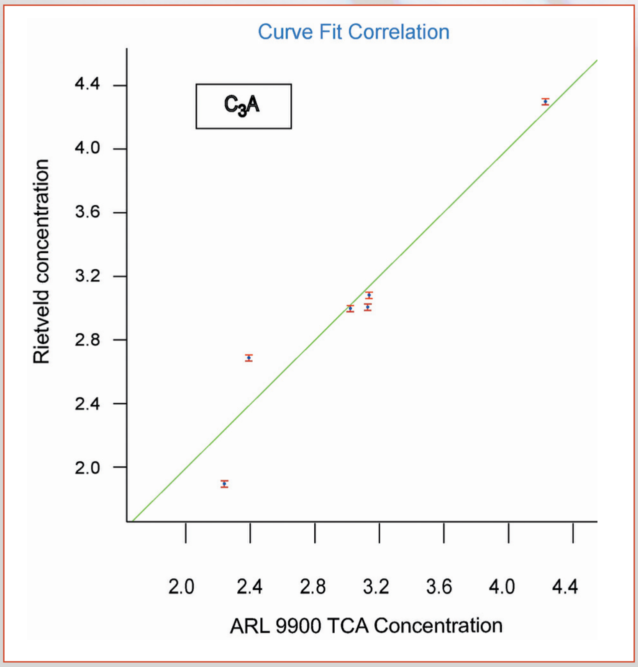


*Figure 5. Calibration curve for $C_3A$ phase in a series of clinkers characterised using Rietveld analysis and measured using ARL 9900 TCA.*

**Table 2. Repeatability obtained with an ARL 9900 Oasis on a cement standard. The concentrations are in %**

| Run | $Al_2O_3$ | CaO | Cl | $Fe_2O_3$ | $K_2O$ | MgO | $Mn_2O_3$ | $Na_2O$ | $P_2O_5$ | $SO_3$ | $SiO_2$ | SrO | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.422 | 67.75 | 0.0119 | 0.330 | 0.173 | 1.635 | 0.012 | 0.021 | 0.046 | 2.039 | 22.05 | 0.110 | 0.185 |
| 2 | 4.421 | 67.77 | 0.0119 | 0.334 | 0.171 | 1.629 | 0.012 | 0.023 | 0.045 | 2.045 | 22.07 | 0.110 | 0.186 |
| 3 | 4.426 | 67.79 | 0.0119 | 0.332 | 0.174 | 1.655 | 0.013 | 0.026 | 0.046 | 2.053 | 22.01 | 0.111 | 0.186 |
| 4 | 4.410 | 67.85 | 0.0123 | 0.332 | 0.170 | 1.634 | 0.012 | 0.021 | 0.046 | 2.043 | 22.05 | 0.111 | 0.183 |
| 5 | 4.441 | 67.81 | 0.0118 | 0.335 | 0.172 | 1.651 | 0.012 | 0.022 | 0.046 | 2.049 | 22.04 | 0.111 | 0.188 |
| 6 | 4.454 | 67.77 | 0.0125 | 0.330 | 0.172 | 1.626 | 0.011 | 0.017 | 0.044 | 2.047 | 22.08 | 0.110 | 0.185 |
| 7 | 4.430 | 67.77 | 0.0121 | 0.333 | 0.171 | 1.628 | 0.012 | 0.028 | 0.045 | 2.050 | 22.10 | 0.111 | 0.186 |
| 8 | 4.407 | 67.82 | 0.0122 | 0.330 | 0.172 | 1.638 | 0.013 | 0.025 | 0.049 | 2.046 | 22.02 | 0.110 | 0.186 |
| 9 | 4.436 | 67.80 | 0.0126 | 0.335 | 0.172 | 1.628 | 0.012 | 0.020 | 0.046 | 2.052 | 22.08 | 0.113 | 0.189 |
| 10 | 4.431 | 67.82 | 0.0121 | 0.333 | 0.174 | 1.640 | 0.011 | 0.028 | 0.047 | 2.059 | 22.08 | 0.112 | 0.185 |
| 11 | 4.441 | 67.83 | 0.0120 | 0.328 | 0.174 | 1.644 | 0.012 | 0.024 | 0.048 | 2.053 | 22.08 | 0.110 | 0.187 |
| *Average* | 4.427 | 67.798 | 0.012 | 0.332 | 0.172 | 1.637 | 0.012 | 0.023 | 0.046 | 2.049 | 22.060 | 0.111 | 0.186 |
| *Sigma* | 0.015 | 0.029 | 0.0003 | 0.002 | 0.001 | 0.010 | 0.0006 | 0.003 | 0.001 | 0.005 | 0.028 | 0.0008 | 0.002 |
| *RSD* | 0.33% | 0.04% | 2.11% | 0.63% | 0.82% | 0.60% | 5.27% | 14.17% | 3.03% | 0.27% | 0.13% | 0.70% | 0.92% |

set of well-characterised clinker samples, which accurately represent the specific process and kiln control parameters of the plant. Using ARL ClinkerQuant™, it is now possible to perform a truly quantitative clinker phase analysis using the Rietveld method as reference. The total analysis time can be optimised, depending on the precision required, to be as low as three minutes.

Figure 4 shows the calibration curve obtained for alite ($C_3S$) phase using the ARL 9900 and based on Rietveld quantification as reference values.

Figure 5 shows another example of correlation for aluminate ($C_3A$) phase ClinkerQuant™ based on the Rietveld method as reference.

These results attest the excellent correlation between concentrations obtained using the Rietveld method, and the intensities measured using ARL 9900 Total Cement Analyser providing an effective and intelligent solution to perform quantitative analysis in a process environment.

**Table 3. Typical limits of detection for various elements on an air filter obtained using ARL QUANT'X**

| Element | Limit of Detection $ng/cm^2$ |
|---|---|
| Cl | 7 |
| Cr | 3 |
| Zn | 2 |
| As | 1 |
| Cd | 10 |
| Hg | 3 |
| Pb | 2 |

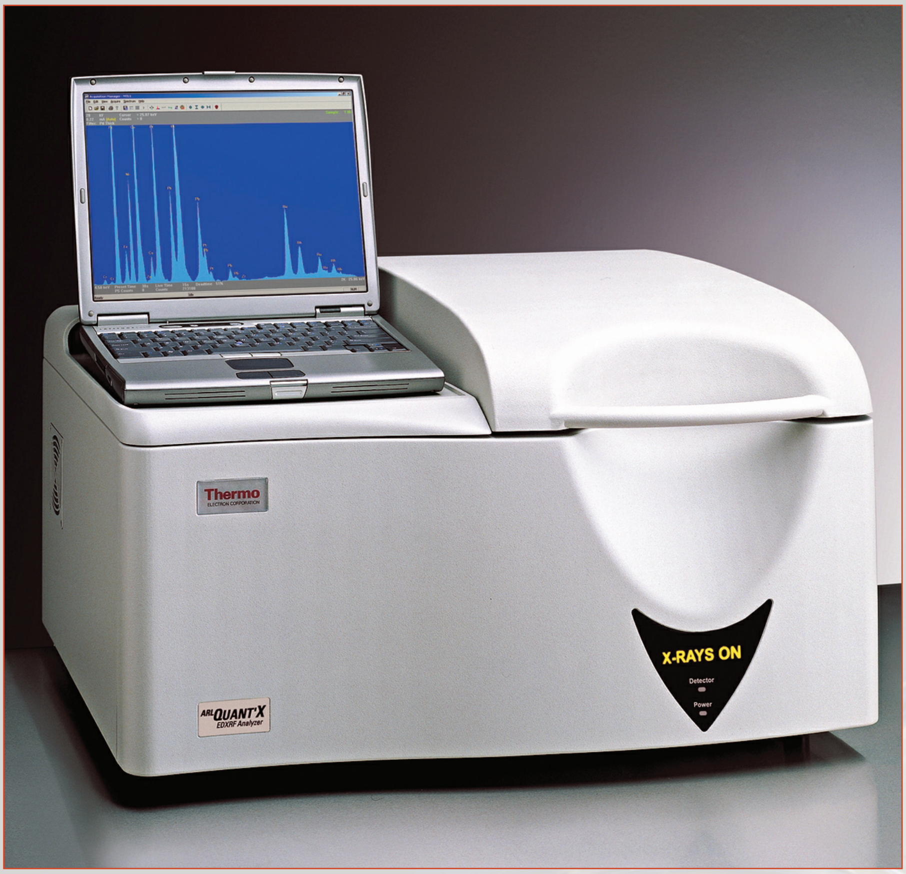


*Figure 6. ARL QUANT'X - high performance EDXRF for non-routine analysis.*

## Handling difficult samples

Energy Dispersive XRF instruments present many advantages when dealing with difficult and 'dirty' samples, in terms of ease of use, operational simplicity and sample handling. For example, analysis of air filters for environmental control, and the screening of difficult samples (e.g. slurries or heterogeneous materials, organic waste and other complex matrices) are more easily accomplished with a benchtop EDXRF instrument. Indeed, such an instrument lightens the analytical load on the mainframe X-ray instrument which is usually dedicated to the routine process and quality control tasks.

ARL QUANT'X is a high performance EDXRF system built around a unique Peltier cooled Si(Li) detector coupled with advanced DPP (Digital Pulse Processing) technology. Unlike conventional energy dispersive systems, this unique sealed detector provides exceptional energy resolution and dynamic range for high quality XRF results. In conjunction with selectable primary beam filters, ARL QUANT'X is capable of achieving limits of detection otherwise only possible by complicated polarisers and associated optics.

Figure 6 shows the compact instrument for field transport or placement near the arrival point of waste materials in a cement plant away from the central laboratory.

## Conclusion

New X-ray instruments are designed to meet the ever increasing demand for more cost effective solutions. These range from simple bench-top EDXRF instruments for the analysis of all kinds of materials generally used for incineration and fuel substitution to integrated XRF-XRD instruments. The cement industry, therefore, has a spectrum of intelligent solutions to choose from, depending on analytical requirements, know-how available in the laboratory, and the degree of flexibility needed.

This article has explored some of the possible scenarios. Cost effective WDXRF instruments are available now for small cement plants and grinding stations, for an uncompromising analysis. Integrated XRF-XRD systems are available at mid power and high power to perform truly quantitative analysis of oxides and clinker phases closer to the process, with minimal demand for support and expertise. An innovative method of clinker phase quantification has been established for process control situations.

Finally, central laboratories where there is know-how and the need for full flexibility to meet the 'unknowns' can always exploit the stand-alone XRD system.