# XRF AND XRD BASED SOLUTIONS

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## INTRODUCTION

The control of chemical and mineralogical compositions of both intermediate and finished products, as well as of raw materials, is of paramount importance to the cement industry. This is even truer today as fierce competition grows and cement prices drop, meaning that high quality analyses are required during the entire production process. Currently, determination of chemical composition and free lime are well-established methods, while full phase quantification is becoming a more popular tool for process optimisation. Modern technology no longer requires highly trained specialists to operate X-ray fluorescence (XRF [a method to determine elemental composition]) and X-ray diffraction (XRD [a method to determine phase composition]) systems. This allows ever easier implementation of these reliable and advanced methods in the entire production process

*Figure 1. X-ray spectrometer S4 EXPLORER and diffractometer D4 ENDEAVOR integrated into an automated laboratory.*

## XRF AND XRD ANALYSIS THROUGHOUT THE ENTIRE PROCESS

The basis of modern cement plant control is chemical analysis performed by XRF, providing vital information about different process steps.

The production process begins with the analysis of various raw materials. These can be quarry materials or alternative materials such as slags, industrial waste, or others. From those materials the oxide compositions are determined via XRF. In order to get reliable and accurate results, the samples need to be prepared either as pressed pellets or fused beads. Both sample preparation procedures can be automated in case high sample throughputs are required.

For the analysis of raw materials sequential or simultaneous wavelength-dispersive X-ray fluorescence (WDX) spectrometers are typically used. The simultaneous WDX systems have a fixed configuration for a certain number of elements. As they measure all elements at the same time they achieve higher sample throughputs than sequential systems. However, when the X-ray tube is sitting above the sample, no liquid or loose powder samples can be analysed.

## ALTERNATIVE FUELS

Besides the standard raw materials, an increasing number of cement plants use alternative fuels to reduce production costs. However, these materials contain additional trace elements that need to be quantified, as they may have a negative or positive impact on the production process or environment[1]. The need to analyse more elements in a wider range of sample types and concentration ranges requires the use of powerful sequential XRF spectrometers, such as the S4 PIONEER (4 kW) or S4 EXPLORER (1 kW) from Bruker AXS.

When dealing with a large variety of alternative fuels, calibrations typically fail as elements, concentration levels and matrix types vary. The reasons for this are the lack of reference samples or important elements such as heavy metals or halogens. In those cases, pre-calibrated methods such as the 'OilQuant' from Bruker AXS easily extend the range of analytical routines. This is a universal calibration using unique variable alpha matrix correction software, which is an option with any of the company's spectrometers. The software corrects for matrix affects over a wide concentration range. With 'OilQuant', a large variety of alternative fuels, such as used oils, paints, diesel, gasoline, and glues, as well as waste plastic materials, can be fully quantified by just analysing the sample. A specific calibration carried out by the user is not required.

## RAW MEAL ANALYSIS OF PRIMARY IMPORTANCE

The control of the chemical composition of the raw mix is of primary importance to ensure the efficient operation of the kiln, and ultimately the quality of the finished cement. Wavelength-dispersive (WDX) and energy dispersive (EDX) X-ray fluorescence instruments have been used for many years to measure the

*Figure 2. The S2 RANGER with autosampler.*

proportion of the oxides of aluminium (Al), silicon (Si), calcium (Ca) and iron (Fe) and hence to calculate the lime saturation factor (LSF), silica ratio (SR) and other modulii needed to control the mixing process. However, when the best analytical performance for oxides of sodium (Na) and magnesium (Mg) are needed, the use of WDX spectrometers is mandatory.

Traditionally, composite samples are taken periodically from the process line and then analysed as pressed pellets with a XRF spectrometer located in the central production laboratory. However, when the mineralogy of raw materials varies over a very wide range, the samples need to be prepared as fused beads in order to achieve accurate quantifications. In larger cement plants, sample taking, sample transport to the central laboratory, sample preparation and sample analysis via XRF are fully automated to achieve accurate, reproducible results and maximum sample throughputs.

When much higher sampling and analysis frequencies are required, the raw mix control is carried out by dedicated fully automated EDX spectrometers located close to the raw mill (on-stream or on-line analysers). A composite sample is taken up to 12 tph and is analysed as compacted powder or pressed pellet. When grain sizes vary, the raw meal is ground before analysis giving more accurate results.

Currently these dedicated EDX systems only quantify the four main oxides: $Al_2O_3$, $SiO_2$, CaO, and $Fe_2O_3$ under He atmosphere. More powerful EDX systems such as the new S2 RANGER from Bruker AXS can reliably quantify additional oxides such as MgO, $SO_3$ and $Mn_2O_3$ (Table 1 shows the reproducibility). The analysis is performed under a vacuum atmosphere, reducing the costs of operation significantly. Due to its enhanced analytical performance, the S2 RANGER can also be used as a true backup system for various applications such as alternative fuels.

In addition, Bruker AXS also offers the S4 PIONEER (4 kW) and the S4 EXPLORER (1 kW) sequential WDX analysers. The first of these allows very high sample throughputs and has the best detection limits (LOD) for light elements. The second is very similar in performance needing slightly longer measurement times, but no detector gas or water cooling, which results in minimum cost of ownership. All spectrometers were designed for easy use in the cement environment and seamless integration into any automated laboratory.

## CLINKER ANALYSIS

Though clinker quality is governed more by its mineralogy and less by its elemental composition, the determination of the chemical composition is well established. Representative samples are taken and analysed with a calibration. The results are used to estimate the clinker phase composition applying the Bogue calculations. Other fast methods for monitoring kiln operation were not available in the past.

Complementary to chemical analysis, many plants determine the free lime content in clinker samples using XRD. The samples are ground, pressed and then analysed with a simple calibration. The free lime results are used together with the estimated phase composition based on Bogue to optimise kiln operation.

In the past, full phase analysis via XRD was not possible due to several physical effects. These make a calibration for clinker and cement phases nearly impossible[2]. Now the D4 ENDEAVOR, a full diffractometer, and the TOPAS BBQ software from Bruker AXS allow the fully automatic quantification of

Table 1. Reproducibility of a typical raw meal sample measured with the S2 RANGER in 200 sec measurement time

| | MgO (%) | $Al_2O_3$ (%) | $SiO_2$ (%) | $SO_3$ (%) | $K_2O$ (%) | CaO (%) | $Mn_2O_3$ (%) | $Fe_2O_3$ (%) |
|---|---|---|---|---|---|---|---|---|
| Average (%) | 1.14 | 3.13 | 17.19 | 0.320 | 0.680 | 40.34 | 0.137 | 2.28 |
| Std. Dev. Abs. (%) | 0.07 | 0.03 | 0.06 | 0.003 | 0.025 | 0.09 | 0.004 | 0.01 |
| R.S.D. (%) | 6.5 | 1.0 | 0.4 | 1.0 | 3.7 | 0.2 | 3.1 | 0.5 |

Table 2. TOPAS quantification results of the NIST clinker RM 8488 (values in wt.%)

| | TOPAS BBQ average and standard deviation | NIST average and standard deviation |
|---|---|---|
| Alite ($C_3S$) | 64.77 (0.36) | 64.97 (0.56) |
| Belite ($C_2S$) | 19.51 (0.28) | 18.51 (0.58) |
| Aluminate ($C_3A$) | 4.04 (0.44) | 4.34 (1.35) |
| Ferrite ($C_4AF$) | 11.71 (0.43) | 12.12 (1.50) |

clinker phases. Together with the company's fast VÅNTEC-1 detector, full analysis takes only a couple of minutes, fulfilling requirements for process control. When sample preparation is optimised the same clinker pellet analysed with XRF can be used for phase determination.

TOPAS BBQ, meanwhile, is the leading Rietveld software package used by all major cement companies (Table 2). In contrast to classical calibration-based quantifications, the Rietveld method is standardless, requiring a full diffractometer. As TOPAS BBQ was developed for the needs of the cement industry, the analysis can be performed by any operator. Expert knowledge is not necessary. For the user in the cement plant, this means that full phase quantification is obtained by simply loading the sample and pushing the start button. This makes it easier than ever to implement XRD into quality control. Details of this powerful method are described in reference 3.

The new VÅNTEC-1 detector (Figure 3) was designed with the high speed requirements of the cement industry in mind. The one-dimensional detector based on proprietary Microgap technology outperforms existing technologies with its excellent high-speed and very good signal-to-background ratio. The VÅNTEC-1 can be fitted into any diffraction system of Bruker AXS, without the need for additional infrastructure such as detector gas.

The combination of fast detectors and Rietveld software makes full phase analysis available. It allows cement manufacturers a better understanding of the kiln process. One example is the increasing use of alternative fuels. This can change the clinker, and hence the cement properties, dramatically. Only when these undesirable properties are quickly monitored via XRD, can corrections be made in order to obtain constantly high clinker qualities[1,4].

## CEMENT ANALYSIS

In the final step of Portland cement production raw materials such as gypsum, gypsum/anhydrite mixtures or other materials are ground up with cement clinker in order to get precisely specified cement properties. Similar to clinker, the performance of cement is governed by the mineralogy and less by the elemental composition.

During the grinding procedure, the temperature of the mill feed can elevate leading to partial dehydration of the gypsum phase ($CaSO_4 \cdot 2H_2O$) to hemihydrate ($CaSO_4 \cdot 1/2H_2O$) (also named bassanite) or even anhydrite ($CaSO_4$). As all sulfate phases do considerably differ in both solubility and reactivity, the degree of dehydration has a direct effect on the setting behaviour. Knowledge about the absolute phase abundance of the sulfate phases in cements therefore allows monitoring and control of the cement mill operation.

However, in the past an appropriate method was unavailable in order to determine the cement phases accurately. Quality control is well established via XRF spectrometry, often by applying quality standards such as ASTM C114-03 or EN 197. Pressed pellets of

*Figure 3. The VÅNTEC-1 detector.*

representative samples are analysed via calibration to determine the typical cement oxides plus the total sulfur content.

The accurate and reliable monitoring of the sulfate phases, plus all other cement phases, can be achieved via X-Ray diffraction using TOPAS BBQ. Applying this new analysis tool will ultimately result in a much better control of the cement mill operation and hence in better cement qualities at reduced cost.

## CONCLUSION

In partnership with the cement industry, Bruker AXS has developed analytical solutions designed to fulfil the needs of this modern industry. The combination of powerful analysers, precalibrated solutions and intuitive software makes it easier than ever to implement XRF and XRD systems for monitoring process steps.

Though XRF has been in use many years, more valuable applications such as the analysis of alternative fuels are becoming established. The consequence is the preferred use of more flexible sequential WDX spectrometers.

Complimentary to XRF, the XRD technique is becoming more popular. Besides the clinker and cement phase analysis, X-ray diffraction has the potential to analyse raw materials such as gypsum and other intermediate products. The full phase quantification will lead to a better understanding of the production process resulting in a better plant efficiency and product quality. ♦

## REFERENCES


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