



Advanced

Introduction

In the modern cement industry, the workflow from raw materials to clinker to cement needs a total approach integrating both chemical and phase analysis at different steps. With pioneering technology, tools and analytical methods have been developed to help the industry meet new challenges and requirements using both XRF and XRD techniques.

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describe how
integrated
chemical and
phase analysis
can be used
to meet the
analytical
challenges of
the cement
industry.

Analysis

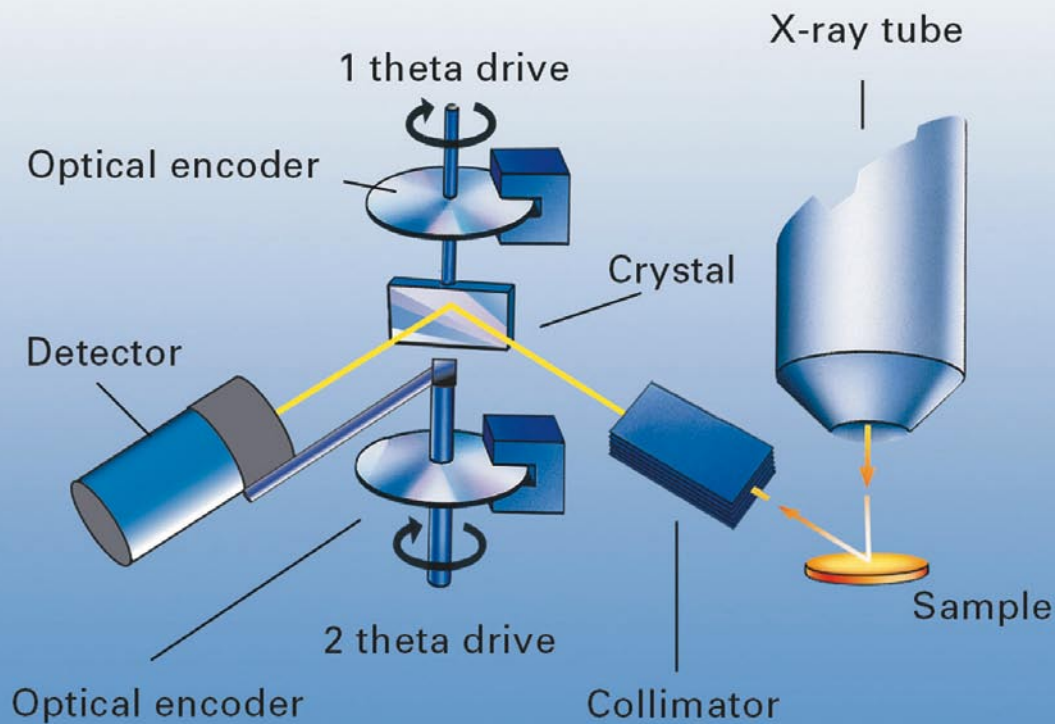


Figure 1. The goniometer of a WDXRF instrument.

The industry has come a long way in “exploiting” XRF capabilities for the chemical analysis of all kinds of materials beyond the basic oxides. In addition, online implementation of X-ray diffraction as a routine tool for the analysis of free lime, clinker phases and additives in cement is becoming more practical and reliable. It is therefore clear that most cement plants are taking an integrated approach where the analytical needs are evaluated as a function of XRF and XRD capabilities and the available expertise.

Fast XRF analysis

The first requirement in every cement laboratory

is to determine the concentration of the following oxides/elements: CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, SO₃, K₂O, Na₂O, P₂O₅ and Cl in raw meal, clinker and cement. The technique of choice for such analysis is X-ray Fluorescence (XRF) because it is fast, requires only simple sample preparation (grinding and pressing) and provides high precision analysis.

Typically, the goniometer of a wavelength dispersive XRF instrument will allow such analysis within a couple of minutes (Figure 1). A counting time of 6 - 10 s per element/oxide is typical, even for medium power instruments of 2500 W or 1200 W respectively. As can be seen in Table 1, the repeatability of analysis using such short analytical conditions

is good and it can be improved for any oxide/element by increasing its specific counting time. Instruments with mid-power levels (1200 W or 2500 W) also present the advantage of not requiring an external water chiller.

Phase analysis for better process monitoring

In addition to the oxide composition of raw materials and products, the cement industry requires an increasingly comprehensive analysis of various phases or compounds. This increased need for chemical and phase analysis in process and quality control has been the reason for the development of instruments that perform both XRF and XRD techniques. In addition to the routine online analysis of key elements, such

Table 1. Repeatability of analysis at 2500 W using only 6 s counting time per element/oxide with a goniometer										
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	Cl
Run no.	(%)									
1	63.78	20.46	5.23	2.88	2.76	3.43	0.928	0.279	0.295	0.0193
2	63.79	20.45	5.26	2.88	2.74	3.42	0.933	0.277	0.299	0.0198
3	63.82	20.42	5.25	2.87	2.77	3.42	0.934	0.283	0.294	0.0201
4	63.75	20.41	5.26	2.89	2.75	3.42	0.934	0.279	0.296	0.0205
5	63.81	20.46	5.22	2.89	2.74	3.43	0.935	0.288	0.298	0.0202
6	63.81	20.46	5.25	2.89	2.77	3.44	0.935	0.277	0.299	0.0199
7	63.81	20.49	5.24	2.88	2.76	3.43	0.931	0.285	0.297	0.0196
8	63.86	20.47	5.25	2.87	2.78	3.42	0.937	0.289	0.302	0.0204
9	63.81	20.46	5.23	2.88	2.74	3.43	0.932	0.286	0.301	0.0202
10	63.79	20.49	5.25	2.88	2.74	3.42	0.928	0.287	0.296	0.0201
Average	63.80	20.46	5.24	2.88	2.76	3.43	0.933	0.283	0.298	0.0200
Std. dev.	0.029	0.026	0.013	0.007	0.015	0.007	0.003	0.005	0.003	0.0004

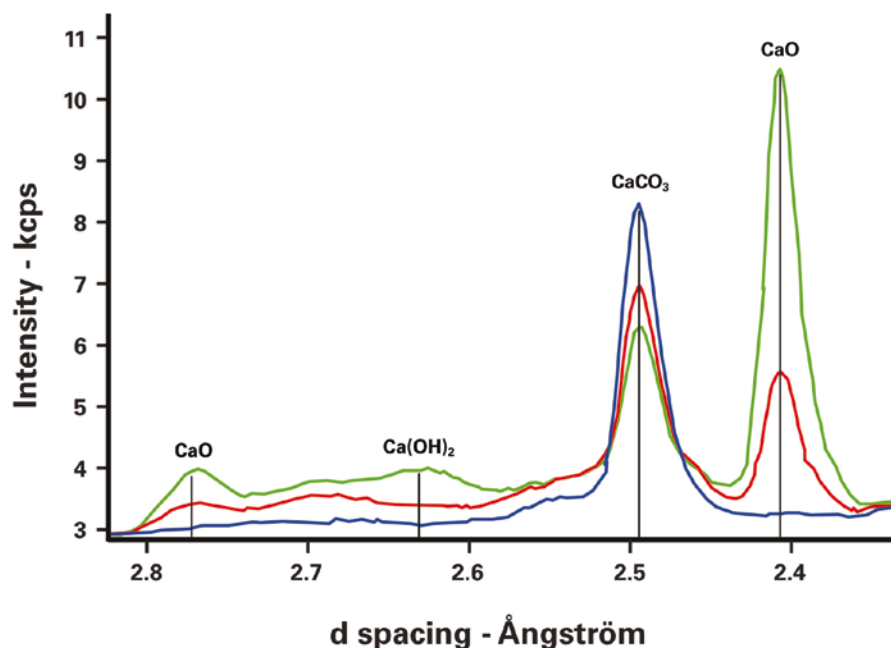


Figure 2. Scans on a raw meal and two hot meals showing the decarbonation process.

an integrated XRF-XRD instrument is capable of covering, without compromise, several phases that can be useful for monitoring the production process.

One of the applications for such an instrument is the measurement of hot meal in order to control the decarbonation level in the various cyclone stages.

During the heating up of the raw meal in the preheating cyclones, the CaCO_3 phase will gradually transform into CaO (as CO_2 escapes due to heating). Figure 2 shows the scans taken on three raw meal samples at various stages of heating: in blue, the sample is cold, there is no CaO . At the first stage of the preheater, the calcium carbonate has partially transformed into CaO (red scan). At a later stage in the cyclones, the calcium carbonate has transformed even more into CaO (green scan).

Another essential application for kiln control is the determination of free lime in clinker. This allows monitoring of the burning conditions in the kiln, because free lime reacts with belite ($\text{C}_2\text{S} - 2\text{CaO}\cdot\text{SiO}_2$) at temperatures above 1350°C to form alite ($\text{C}_3\text{S} - 3\text{CaO}\cdot\text{SiO}_2$). A rise of free lime content indicates that the temperature is not high enough in the kiln, which may indicate clogging or other problems. A drop of free lime shows that the temperature in the kiln is high or too high, which indicates too much fuel usage. Furthermore, clinker with a low free lime level is hard to grind and necessitates more energy during milling. At the same time, high alite levels can help to achieve a high final resistance of cement. Therefore, it is essential to control the free lime level in the clinker and keep it balanced, typically at around 1 - 1.5%.

Bad burning conditions in the kiln can be detected through higher free lime levels, which are also not desirable in view of the higher volume expansion that it produces during hydration of cement.

The free lime determination can be completed in 10 – 40 s using the ARL 9900 Total Cement Analyzer, while a titration with ethylene glycol would take 30 - 45 minutes. As shown in Table 2, the repeatability of analysis is excellent even at lower content of free lime (0.67% in this case) and the free lime result is delivered at the same time as the element/oxide analysis performed by the XRF portion of the instrument.

As previously mentioned, controlling the free lime level in clinker is an indirect way to determine the alite and belite balance, but with an integrated XRD system it is possible to directly determine

Table 2. Repeatability test for free lime and usual oxides in clinker (Thermo Scientific ARL 9900 Total Cement Analyzer - 40s counting time on free lime and 40s counting time on each oxide)

Run no.	XRD	XRF							
	Free lime	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	SO ₃
1	0.67	65.54	21.42	5.59	3.97	1.55	0.68	0.58	1.01
2	0.68	65.52	21.41	5.59	3.96	1.55	0.68	0.58	1.00
3	0.67	65.52	21.41	5.59	3.96	1.55	0.68	0.58	1.00
4	0.66	65.50	21.40	5.58	3.96	1.55	0.68	0.58	1.00
5	0.67	65.50	21.39	5.58	3.96	1.55	0.68	0.58	1.00
6	0.66	65.52	21.41	5.58	3.96	1.55	0.68	0.58	1.00
7	0.66	65.52	21.41	5.59	3.96	1.54	0.68	0.58	1.01
8	0.67	65.51	21.41	5.58	3.96	1.55	0.68	0.58	1.00
9	0.67	61.51	21.41	5.59	3.96	1.55	0.68	0.58	1.00
10	0.65	65.50	21.39	5.59	3.96	1.55	0.68	0.58	1.00
Average	0.67	65.51	21.41	5.59	3.96	1.55	0.68	0.579	1.00
Std. dev	0.007	0.014	0.011	0.009	0.004	0.003	0.001	0.002	0.001

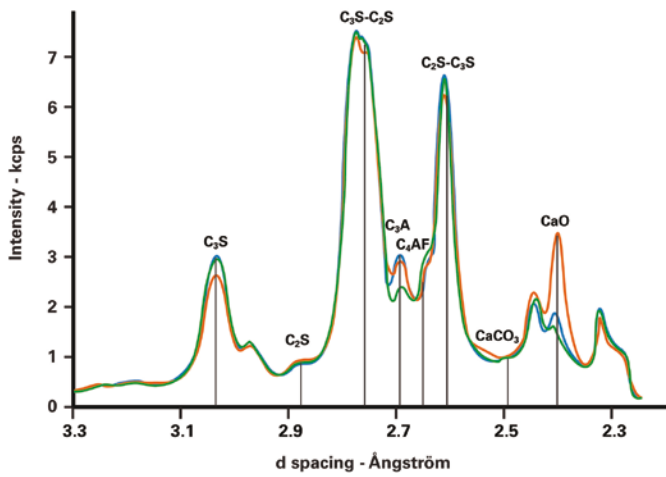


Figure 3. Scans on three different clinkers showing the typical clinker phases, using the compact integrated XRD system.

Table 3. Repeatability of analysis of clinker phases

Counting time	60 s	60 s	15 s	15 s	10 s
	Alite	Belite	Aluminate	Ferrite	Free lime
Run no.	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	CaO free
1	67.42	15.52	3.26	12.65	0.45
2	67.68	15.9	3.18	12.56	0.44
3	67.57	15.61	3.17	12.62	0.45
4	67.43	15.28	3.21	12.61	0.45
5	67.8	15.19	3.17	12.68	0.44
6	67.62	15.71	3.23	12.76	0.45
7	67.71	15.59	3.22	12.65	0.45
8	67.57	15.38	3.25	12.66	0.44
9	67.37	14.92	3.27	12.79	0.44
10	67.63	15.37	3.22	12.77	0.44
Average	67.58	15.45	3.22	12.68	0.45
Std. dev.	0.14	0.28	0.04	0.08	0.007

these two phases as well as the two other main phases of clinker, C₃A (3CaO·Al₂O₃) and C₄AF (4CaO·Al₂O₃·Fe₂O₃)^{1,2}.

These clinker phases are usually calculated from the main oxides composition using the Bogue formulae. These calculations have proven to be approximate, as they do not necessarily reflect potential problems in the clinker composition. Figure 3 shows the various XRD peaks that are used to establish calibration curves for this determination.

As shown in Table 3, good repeatability is obtained even when using relatively short counting time.

Other applications for such an integrated XRF-XRD instrument, which includes a Compact XRD system, comprise the determination of quartz in raw materials and raw meal (Figure 4), and the determination of filler additions in cement, such as limestone³, pozzolan or metallurgical slags, although the latter is usually determined by XRF on the S Kβ satellite peak.

Phase determination

In addition to the routine online analysis of key elements and phases, there are additional phases that may be beneficial to control during cement production, for example periclase in clinkers, C₃A cubic vs C₃A orthorhombic differentiation, or gypsum phases in cement.

For these additional needs, a fully-integrated X-ray diffraction system with wide angle coverage is required⁴. Such an integrated XRF-XRD instrument is capable of covering all additional or occasional analytical requirements for a full phase analysis. This new technology can provide complete quantitative phase analysis in a few minutes, in addition to the chemical analysis of all usual elements or oxides. The quantitative phase analysis can be based either on full pattern method (Rietveld or similar methods) or specific calibration methodology. Figure 5 indicates a number of such applications within a typical cement

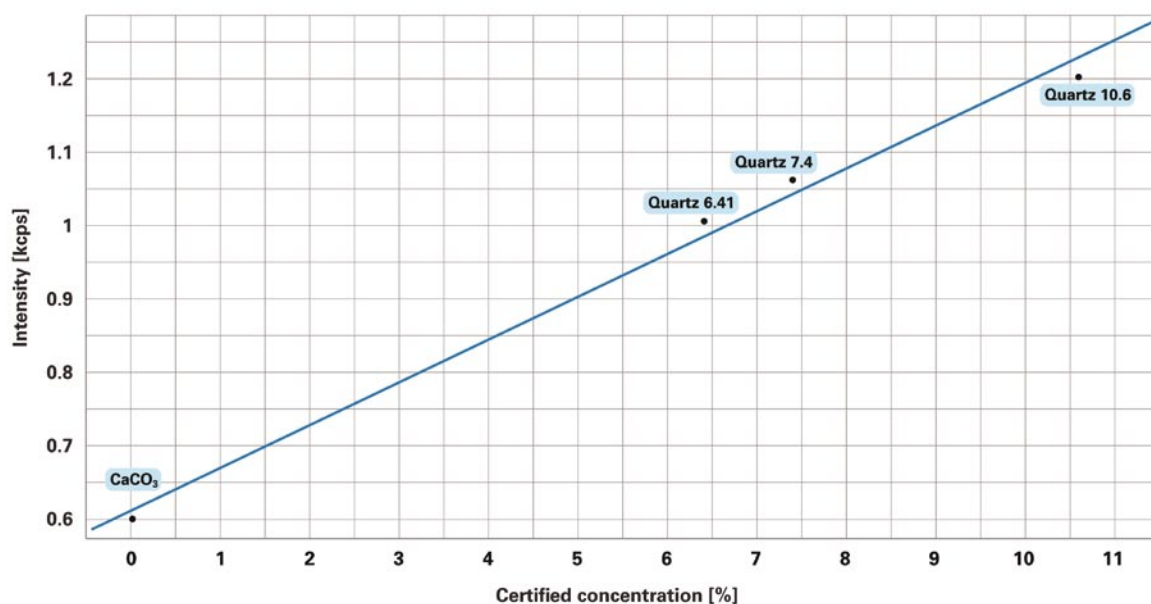


Figure 4. Regression for determination of quartz in raw meal using the Total Cement Analyzer.

process. Such an integrated XRF- XRD instrument, called an X-ray Workstation, makes full analysis easier for the operator as the software integrates both the XRF and XRD capabilities (Figure 6). This also means easier user

training, quick commissioning for production purposes and less laboratory floor space compared to two instruments. Thanks to the use of a standardless software module, the XRD data can be obtained without calibration (full pattern

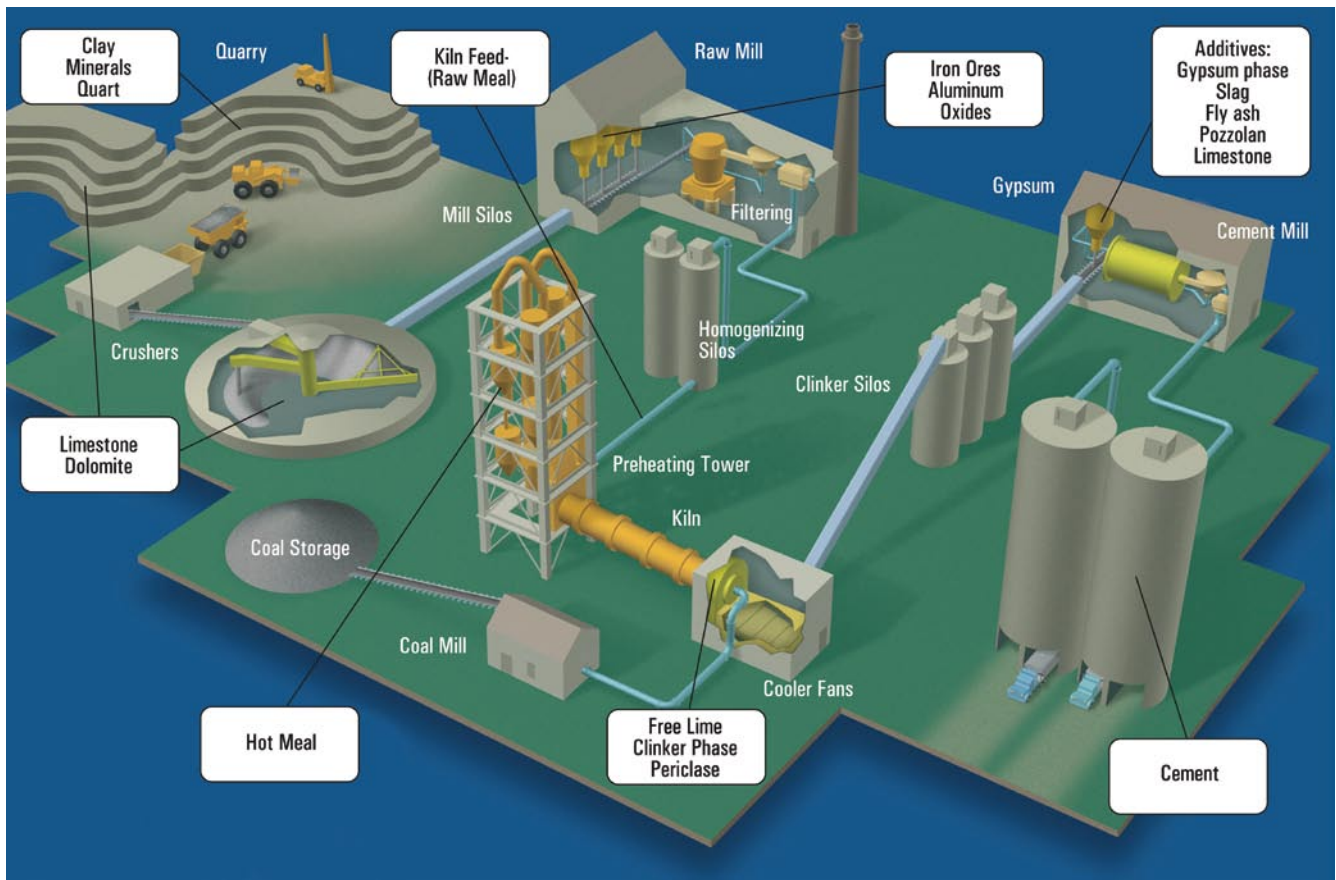


Figure 5. Possible phase analysis applications within a typical cement process.

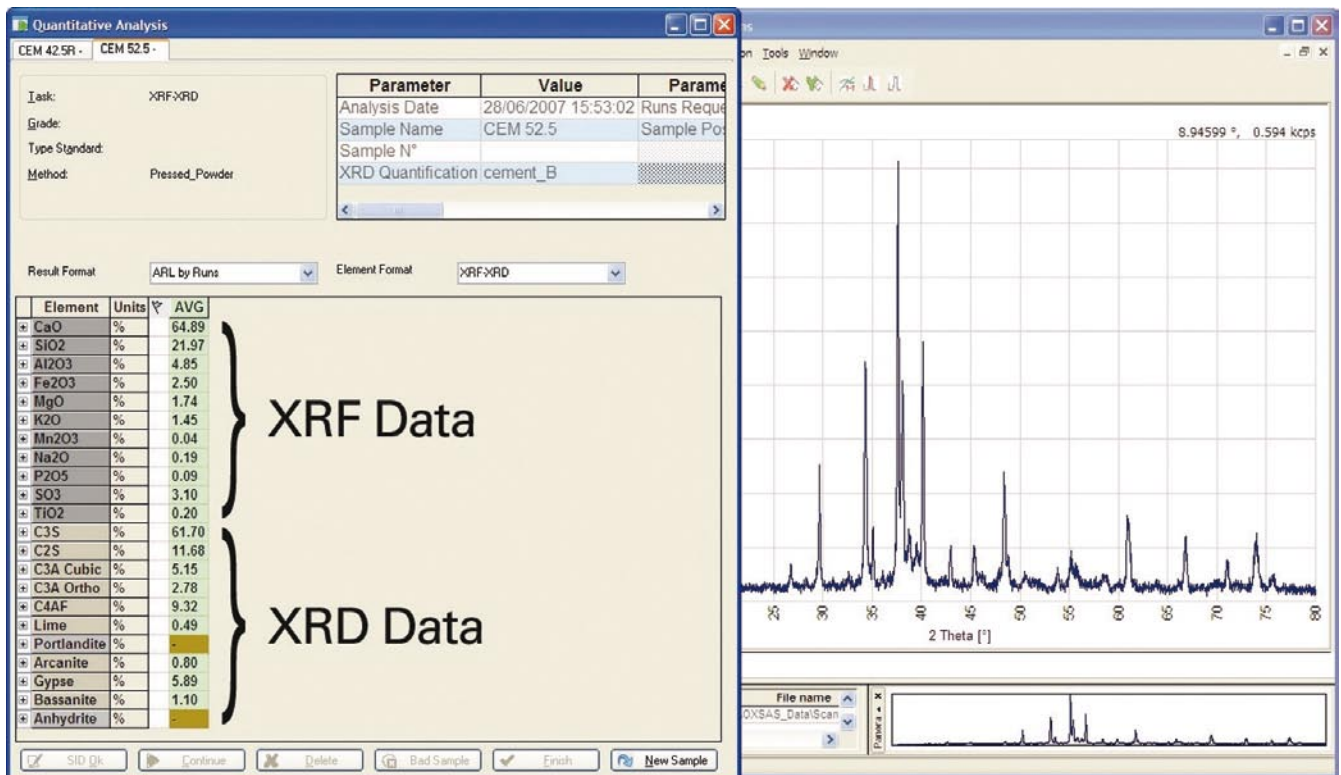


Figure 6. Both XRF and full XRD results are obtained on the same screen without operator intervention.

quantitative determination). However, it is always possible to build a specific calibration curve using a few standards with known concentrations, if preferred, for example for free lime determination. The X-ray Workstation provides very stable and repeatable XRD data thanks to operation under vacuum and the use of a cobalt anode tube for the XRD analysis. The XRF analysis is obtained with a rhodium anode tube. Therefore the instrument can be used as XRF only, or XRD only, or both, without compromise on the performance.


Integration into any process control is quite simple, as the instrument can be linked directly to automatic preparation



Figure 7. ARL 9900 X-ray Workstation linked via transport belt to automatic sample preparation (mill and press).

machines through a transport belt (Figure 7). Such an X-ray Workstation is able to explore new phase analysis applications in cement process control like langbeinite in hot meal to prevent clogging in cyclones, determination of C_3A orthorhombic and C_3A cubic, and determination of gypsum hemi-hydrate (bassanite - $CaSO_4 \cdot 0.5H_2O$) in cement, which may be obtained in case of excessive heat during milling.

Conclusion

In the cement plant laboratory, wet chemistry can be replaced by X-ray diffraction, which provides much faster information, can cover additional tasks and provide complementary information. Both the XRF and XRD information help control the cement production process more comprehensively. An integrated XRF-XRD instrument can provide both results during the same analysis and on the same sample, which prevents the need of an XRD specialist in the laboratory. Full X-ray diffraction can make use of full pattern quantification software (Rietveld or similar) for phase determinations. This type of instrument can also be easily linked to automatic preparation machines to provide a fully automatic analytical solution. 

References

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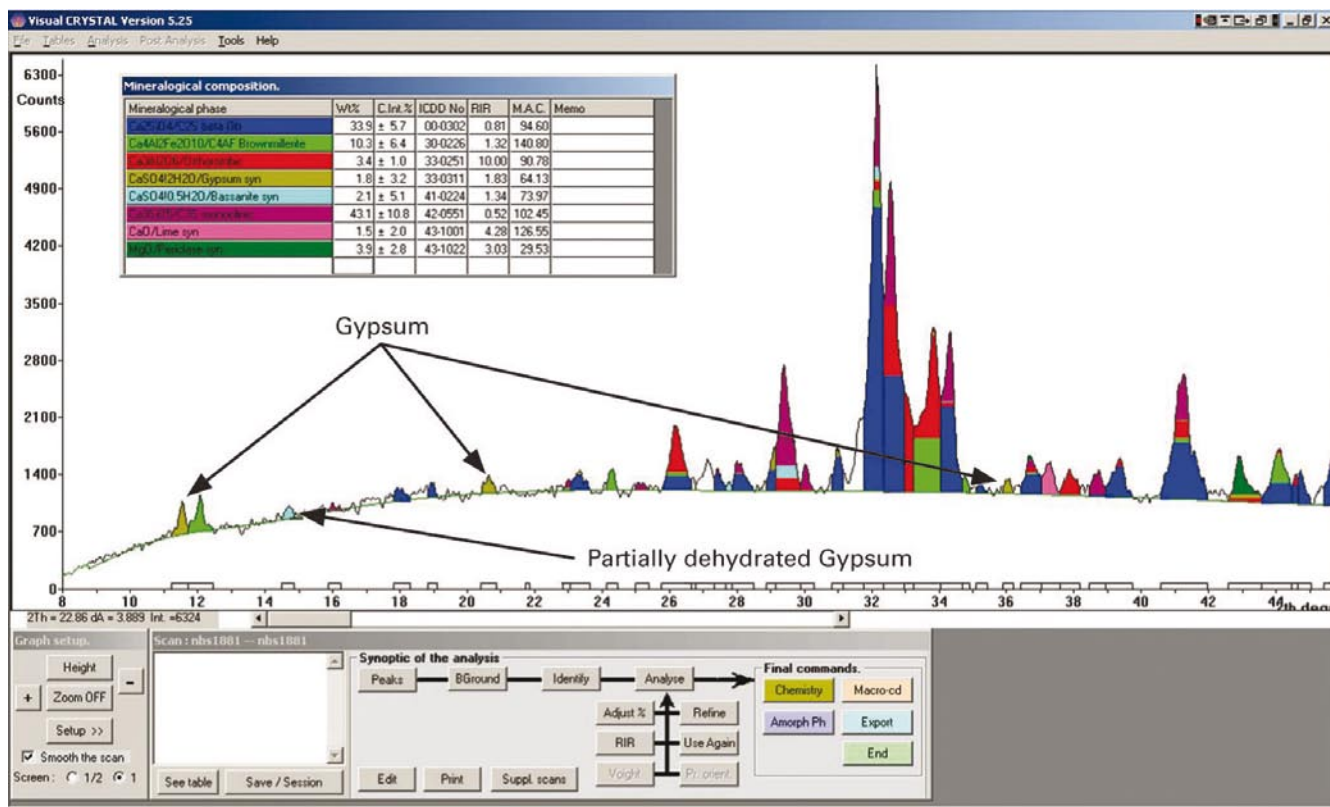


Figure 8. Full diffractogram on a cement specimen with colour coding of the various phases for easier understanding. Gypsum and gypsum hemi-hydrate peaks are shown.