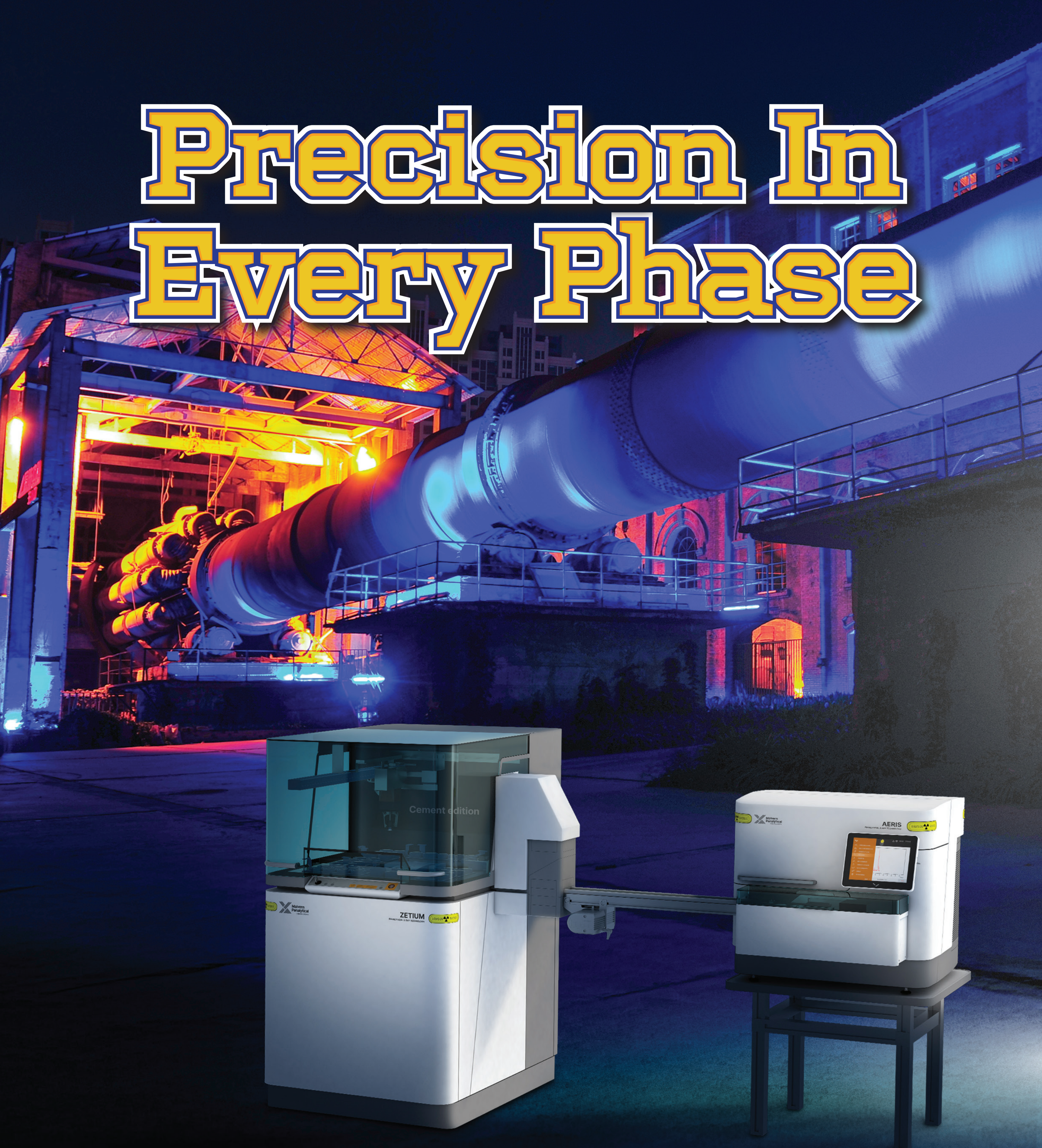
Precision In Every Phase



Dr. Violeta Uricanu, Dr. Matteo Pernechele, and Dr. Murielle Goubard, Malvern Panalytical, explain how XRF and XRD are empowering the cement industry's green transition.

The cement industry is facing one of its greatest transformations. Rising environmental expectations, tightening CO_2 regulations, and the growing use of alternative fuels (AFs) and supplementary cementitious materials (SCMs) are reshaping how producers operate. To remain competitive, cement plants must balance performance, cost, and sustainability – making process insight and control more critical than ever.

In this context, X-ray fluorescence (XRF) and X-ray diffraction (XRD) are indispensable tools for plants determined to optimise quality and efficiency across the entire production chain. These complementary analytical techniques deliver the detailed chemical and mineralogical information needed to make confident, data-driven decisions – from raw mix preparation to clinker production and final cement blending.

Malvern Panalytical's Zetium XRF spectrometer and Aeris XRD system are designed to work seamlessly (independent or as a TWIN combination) within the demanding environment of modern cement plants. Zetium ensures stable, precise elemental analysis for feed, fuel, and product control, while Aeris provides fast, accurate mineralogical quantification to monitor phase development and ensure process stability. Together, they empower quality and production teams to reduce variability, lower energy consumption, and maximise the use of alternative raw materials (ARMs) – all without compromising product performance.

This article explores how the combined use of XRF and XRD strengthens process control and enables successful diversification of production changes from, raw materials down to the next-generation green cements. Real-world XRF and XRD analytical data demonstrate how these technologies help cement producers turn quality and sustainability into tangible business advantages.

Analytical approach and experimental design

Zetium XRF is a wavelength-dispersive, high-power spectrometer, capable of analysing a wide variety of chemical compositions, from the traditional raw materials, clinkers and cements to all new additive types. XRF specimens are prepared either as pressed pellets or fused beads.

Pressed pellets allow quick screening of major oxides (CaO, SiO_2, Al_2O_3, Fe_2O_3), minor oxides (Na_2O and MgO), quantification of chlorine and fluorine down to concentrations below 100 ppm, and evaluation of sulfur content in two separate chemistries: sulfide S^{2-} and sulfate SO_4^{2-}. Mineralogy has a strong effect on XRF calibrations and running pressed pellet analysis requires a good collection of plant-specific standards for each material type. When subjected to fusion, the ensemble of various minerals (alite, belite, clay minerals, etc.) is reduced to a mix of simple oxides diluted into a Li-borate based matrix. While fused bead preparation requires skilled personnel and precision work, the XRF results provide the best accuracy (Figure 1).

Typically, on a Zetium – 2.4 kW spectrometer, full XRF evaluation requires between 2 min. (pressed pellets) and up to maximum 4 min. for fused beads.

Aeris XRD is a system operating in Bragg-Brentano geometry, widely used for mineral phase analysis in cement environments. With its robust and compact design (at only 600 W), Aeris features high-end components, an external sample changer, and automatic Rietveld analysis routines. With Aeris,

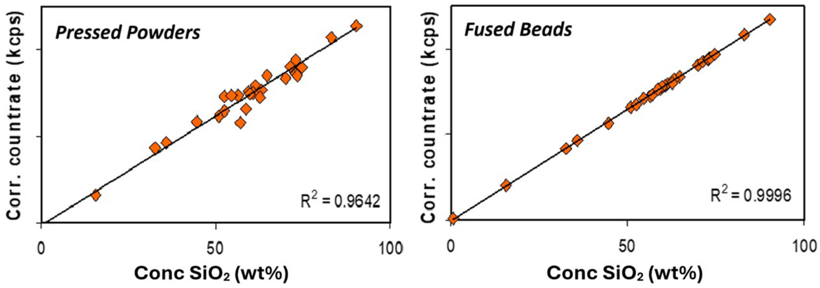


Figure 1. Best quality of XRF calibrations is obtained on fused beads.

Table 1. Compositions of raw materials as determined via XRF on fused beads.

Concentration (%)	Slags			Iron ore	Ash	Mill scale	Bauxite
	GBFS	ACS	DOT				
SiO_2	36.23	36.52	23.60	23.07	42.96	0.17	11.70
Al_2O_3	5.45	6.34	2.84	1.69	19.64	49.53	44.79
Fe_2O_3	3.44	2.40	25.63	73.02	8.68	48.47	22.14
CaO	42.88	41.90	26.79	0.15	2.64	1.60	0.71
MgO	4.76	5.39	5.03	0.05	1.34	---	0.21
SO_3	3.05	2.06	0.43	---	0.22	---	---
K_2O	0.34	0.44	0.27	0.06	2.81	---	0.26
Na_2O	0.41	0.56	0.16	0.01	0.89	---	0.08
TiO_2	0.18	0.25	0.27	0.09	0.77	---	6.47
P_2O_5	0.08	---	0.32	0.06	0.15	---	0.18
Mn_2O_3	0.50	0.32	3.62	0.04	0.07	---	0.09
Cr_2O_3	---	0.04	0.23	---	---	---	---

clinker producers screen the free lime content consistently and much faster than traditional wet chemistry, enabling tighter control of kiln operation and avoiding over- or under-burning. Full mineralogical analysis includes evaluation of:

- Alite polymorphs M1 and M3 – responsible for the early strength development of cement.
- Cubic and orthorhombic aluminates – influencing the setting behaviour.
- Belite phases – connected with the long-term strength development.

Besides surveying clinker quality, cement producers use Aeris to confirm and adjust dosing of different SCMs in blended cements. Aeris can also be used for screening raw and calcined clays from different suppliers.

The most economical way to run X-ray analysis makes use of pressed pellets, preferably made with automated grinding/pressing equipment, so each pellet can go to both XRF and XRD. Fine tuning of grinding (times/speed) and pressing parameters is the first compulsory step to qualify the full method: from initial material to XRF/XRD results. Further, running in compliance with international test methods (like EN 196-2:2025 / ISO 29581-2:2010, for XRF) and according to an iterative cycle of testing, the lab would do daily checks on spectrometer/diffractometer stability and pressed pellet preparation line.

Weekly checks (XRF analysis) are conducted on the fused bead preparation line and control of the pressed pellet results by fused beads.

Quality surveys in cement plants

From the multitude of data available in cement plants using Malvern Panalytical X-Rays equipment, a few examples are selected. Separate or combined, XRF and XRD contribute to process stability, quality consistency and sustainability outcomes under real operating conditions.

XRF results highlight the capability of the Zetium spectrometer to deliver exceptional precision and repeatability in elemental composition, ensuring tight control of major oxides and trace components. In parallel, the Aeris XRD system provided rapid, accurate phase quantification, enabling continuous monitoring of clinker

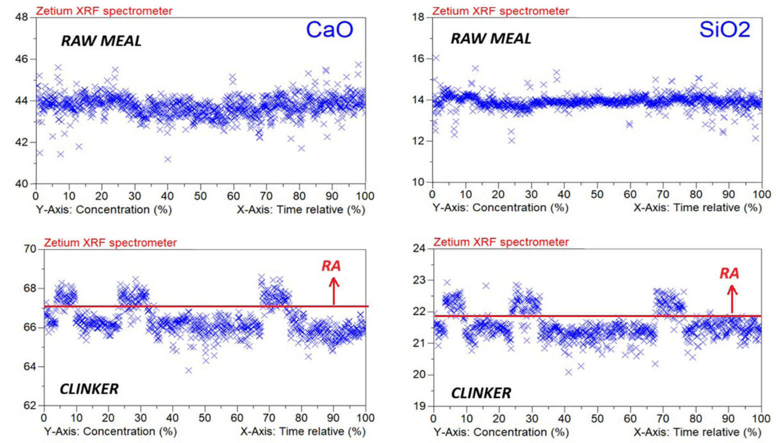


Figure 2. Evolution of raw meal and clinker concentrations (via XRF, on PP).

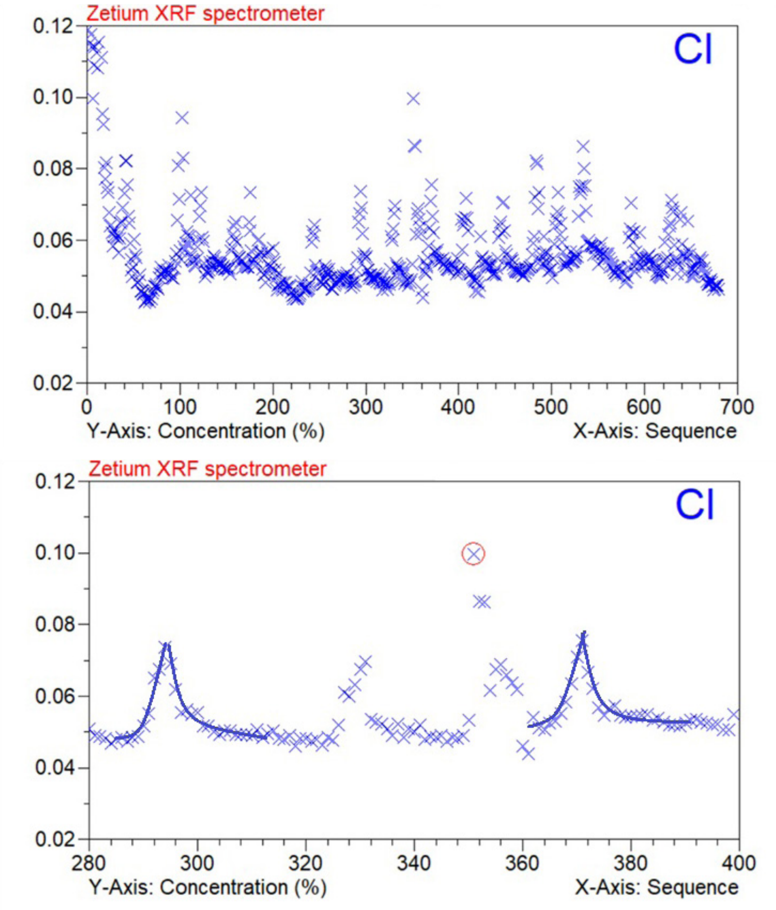


Figure 3. Chlorine evolution in raw meal, when salts are added into formulation. Measurements are done every 2 hours on pressed pellets. (lower image) zoom-in for 10 days time interval.

mineralogy and SCM reactivity. Together, these insights reveal how a fully integrated analytical approach can improve process efficiency, reduce corrective actions and support the production of high-performance green cements.

Improving raw mix, kiln feed, and clinker consistency

Maintaining consistent raw mix chemistry is fundamental to stable kiln operation and clinker quality. With its high precision and long-term stability, the Zetium XRF spectrometer enables rapid adjustment of feed composition, ensuring that key quality modules remain within target limits and process variability is kept to a minimum.

By keeping chemical fluctuations under control, producers can operate closer to optimum setpoints – reducing fuel consumption, improving throughput, and laying a stable foundation for every downstream process.

Surveys of raw meal composition go in parallel with the screening of the clinker and the high sensitivity of the Zetium captures subtle changes in processing parameters.

For example, at cement plant A, during a 3-month period of operation (Figure 2), adjustments of raw meal composition does not show drastic variations of the major oxides but clearly shows the clinker changes between the regular and reduced-alkali (RA) formulations.

Since Na and K salts are more volatile in the chloride form, running the kiln for production of low-alkali clinker at lower burning temperatures is done using additions of $CaCl_2$. These salt additions in the raw meal are traceable via the chlorine – evolution chart (Figure 3). Spikes in Cl values are gradually damping to the target value (~ 0.05 % Cl).

It takes between 24 to 36 hours from the maximum charge until Cl-values return to the setpoint.

Subtle changes in additive type – impact on clinker properties

While cement mixtures with additives are not a novelty, production plants increasingly diversify the raw meal compositions by incorporating between 5 to 15% of ARMs (like slags, fly ash, mill scales, etc.). Composition controls via XRF on pressed pellets may reveal precisely the transfer from one mixture to another.

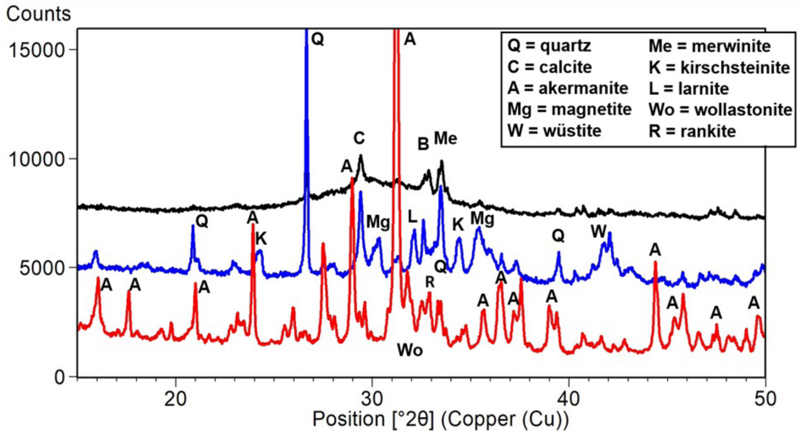


Figure 4. Diffractograms for three slags: GBSF (black), DOT (blue), and ACS (red).

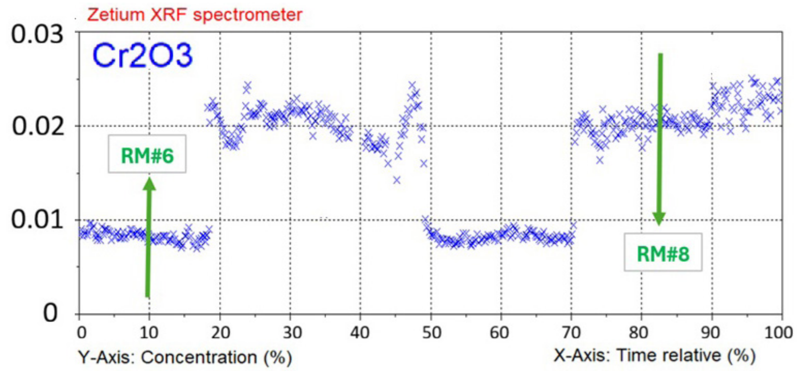


Figure 5. Increased levels of Cr in raw meals at plant B, when DOT slag is used. Vertical lines indicate the time when raw meals #6 and #8 have been taken for XRD analysis.(black), DOT (blue), and ACS (red).

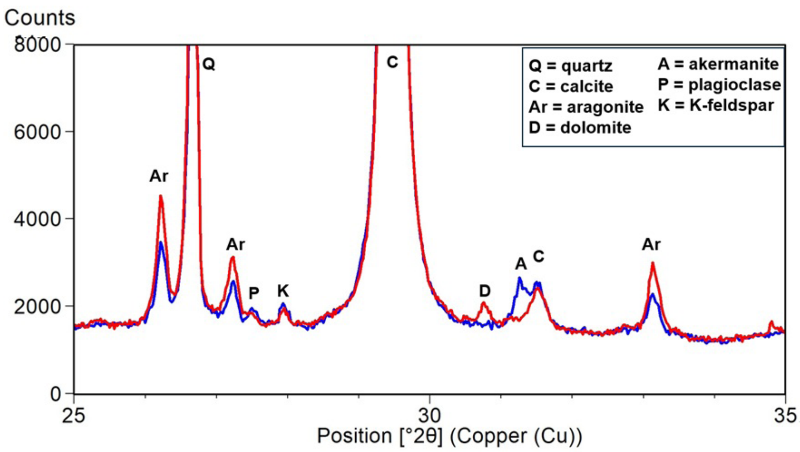


Figure 6. Details in XRD patterns of raw meal #6 (red curve) and #8 (blue curve).(black), DOT (blue), and ACS (red).

As an example, over a 2-year period cement plant B has experienced frequent changes in mixtures while keeping an average of 10% in total ARMs additions to the raw meal. Typical concentrations for their additives are given in Table 1, showing diverse mineralogy (Table 2) with more than 20 distinct phases. Iron ore and mill scale are rich in iron bearing minerals: hematite, wüstite, and magnetite. Meanwhile, from a mineralogical point of view, the three slags used at this plant are extremely different (Figure 4). GBFS- and ACS-slags have a rather similar chemical composition, but GBFS is mostly amorphous, while ACS is rich in akermanite: $Ca_2MgSi_2O_7$ and other high temperature crystalline silicates. DOT (a demetallised steelmaking slag) is rich in iron, present as oxide (magnetite: Fe_3O_4 and wüstite: $Fe_{1-x}O$) but also combined with other elements (srebrodolskite: $Ca_2Fe^{3+}O_5$ and kirschsteinite: $CaFe^{2+}SiO_4$). The combination of XRD and XRF analysis gives a more comprehensive understanding of these additives.

Screening over five different raw meal formulations may not show significant changes for the major oxides, but trace analysis reveals a clear change in the levels of Mn and Cr (Figure 5) when DOT slag is used.

Mineralogical profiling via XRD highlights differences between raw meals in terms of phase types and relative percentages. Calcite (from limestone) remains the dominating mineral, but direct comparison of minor crystalline phases (Figures 6 – 7) would indicate the change to a new formulation. Akermanite is characteristic of the ACS added to formulation #6, while boehmite comes from bauxite added to recipe #8. The content of DOT in raw meal #8 is too small to allow a clear distinction in the XRD pattern of the high-temperature phases seen on the pure DOT.

When additive types are changing, clinker hardness may be affected. As the next section explains, modifications in clinker grindability would also impact XRF/XRD analysis.

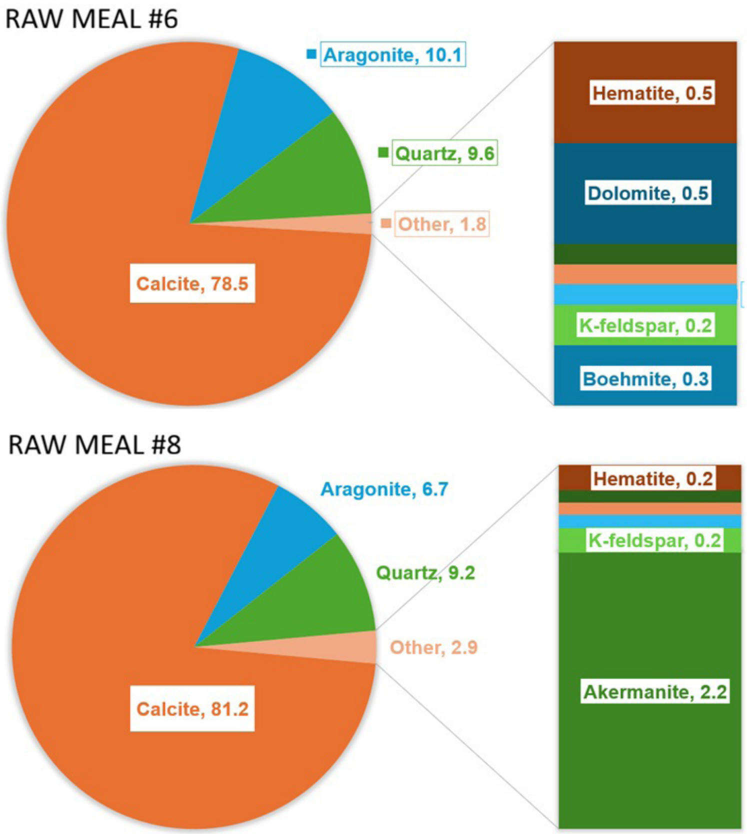


Figure 7. Mineralogical evaluation for two raw meals: #6 and #8 (black), DOT (blue), and ACS (red).

Table 2. Mineralogical composition of raw materials via XRD on pressed pellets.

Slags				**Other additives**				
Phases (%)	GBFS	ACS	DOT	Minerals (%)	Iron ore	Ash	Mill scale	Bauxite
Quartz	1.0	0.6	19.1	Quartz	51.4	8.1	---	0.7
Calcite	1.8	3.4	12.4	Calcite	0.0	3.0	---	0.6
Akermanite	---	65.6	---	Hematite	45.4	1.9	9.3	29.1
Rankite	---	11.3	---	Wüstite	---	---	48.4	---
Wollastonite	---	15.2	---	Magnetite	---	---	42.3	---
Thaumasite	---	3.4	---	Mullite	---	6.7	---	---
Larnite	---	---	18.1	Bohemite	---	---	---	25.1
Srebrodolskite	---	---	13.1	Diaspore	---	---	---	28.6
Kirschsteinite	---	---	19.9	Kaolinite	3.2	---	---	11.6
Bredigite	3.0	---	---	Anatase	---	---	---	4.3
Merwinite	2.9	---	---	Amorphous	---	80.3	---	---
Wüstite	---	---	8.2					
Magnetite	---	---	9.2					
Amorphous	91.3	---	---					

Monitoring clinker quality and free lime stability

Accurate phase quantification with the Aeris diffractometer provides essential insight into clinker mineralogy and free lime content. This allows producers to fine-tune burning conditions, avoid over- or under-burning, and maintain the optimal balance between alite, belite, and aluminate phases for consistent cement performance.

The result is a more predictable and energy-efficient kiln process that ensures every tonne of clinker meets specification – setting the stage for precise control of subsequent blending and SCM optimisation.

With increased variability in raw meal mixtures, if XRD/XRF analysis is combined on the same pellet, grinding optimisation for clinker must be checked on a regular basis.

Changes in clinker hardness may result in sub-optimal analysis data and large artificial fluctuations in compositional results. Rigorously keeping track of changes in the XRF data is recommended and should be done via cross checks between fused beads and pressed pellets results (Table 3).

When biases (PP-FB) for raw meal remain within acceptable limits but those for clinker start to show deviations outside the reliable working regime, that would be the moment to redo the optimisation test.

Keeping the grinding speed constant and varying the grinding time, performing XRF/XRD analysis on multiple pellets will help establish the best option. Examples of variation in XRF and XRD results for such a test are shown in Figure 8.

Optimum pellet preparation for XRF and XRD is different. To reduce grain sizes and minimise mineralogical effects, higher grinding energy is required for materials that will undergo XRF analysis.

Such energy can often destroy the crystalline structures and produce amorphous material. For XRD analysis, as the mineralogical composition needs to be preserved, low grinding energy is better. Analysing the same pellet with XRD and XRF means a compromise on analysis performance. For XRD it is important to avoid over-grinding as the crystalline phases may be destroyed. With increasing grinding energy (see XRD patterns of clinker in Figure 9), intensities of the alite C3S peaks decrease, while the ferrite C4AF remains unaffected, resulting in wrong relative percentages of phases. Over-grinding destroys soft minerals, for example: the free-lime CaO when ground at 1500 rpm (Figure 10). This must be avoided as it makes the XRD analysis unsuitable for quality and process control. The milling speed has more effect than increasing the milling time. For XRD it is preferable to use low milling speeds (700 – 900 rpm) and increase the milling time if needed. High milling speeds (1100 – 1500 rpm) can partially destroy the mineralogy even at a short milling time. When grinding for 90 sec. (Figure 10), the free-lime CaO structure is preserved at 750 rpm, while it is completely destroyed when grinding at 1500 rpm.

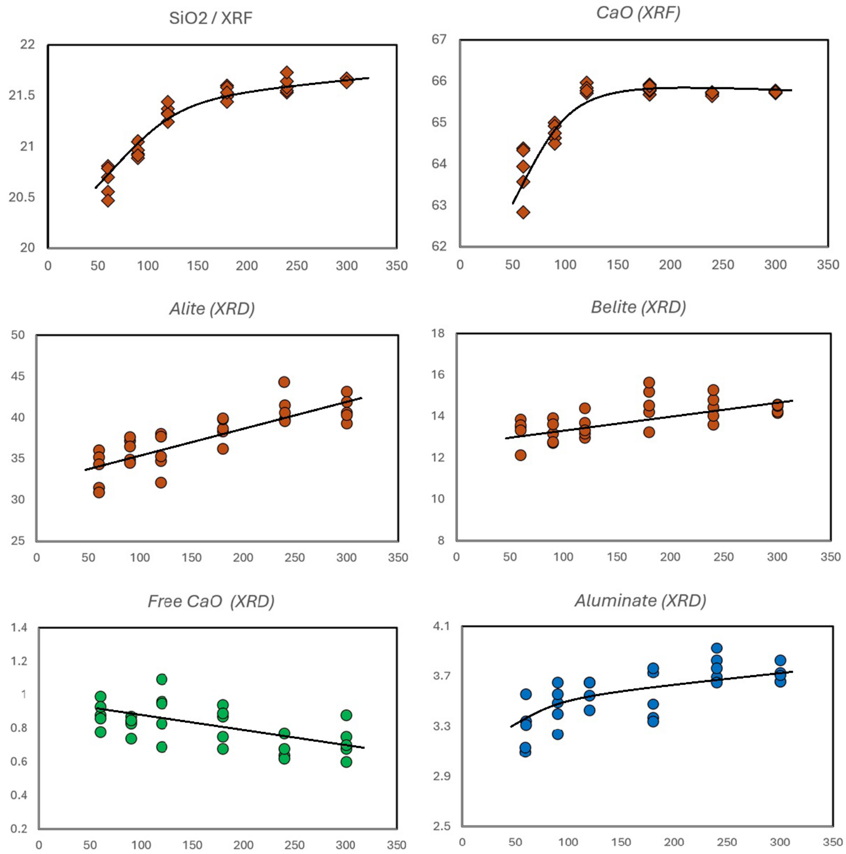


Figure 8: Variability in XRF/XRD results with increased grinding times for clinker, at constant grinding speed.

Table 3. Typical acceptable bias for the XRF measurements on PP-FB.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	P_2O_5	SO_3	K_2O	NA_2O
Raw mix	±0.40	±0.15	±0.15	±0.40	±0.15	±0.05	±0.15	±0.08	±0.08
Cement & clinker				±0.60					

Return on investment: efficiency gains and quality assurance

As the cement industry continues its transition towards low-carbon production, reliable and actionable data remain the foundation of every successful strategy. The combined use of XRF and XRD gives producers the confidence to innovate – optimising raw materials, reducing energy consumption, and increasing the use of alternative materials without compromising quality or compliance. By transforming complex chemistry and mineralogy into clear, real-time insight, these analytical tools help cement manufacturers unlock measurable efficiency gains and strengthen their sustainability performance. ■

About the authors

Dr. Violeta Uricanu is a physicist by education and started her working career in 1991. After 15 years doing research in chemistry related environments, she joined Malvern Panalytical in 2006. Presently, she works as an Application Specialist and Expertise Consultant for X-ray fluorescence, in the Application Competence Center, Almelo, The Netherlands. She provides global technical support for customers using Malvern Panalytical spectrometers in several industrial sectors. Besides trainings, customer demonstrations and feasibility studies, Violeta is involved in development projects aiming to extend the capabilities of XRF beyond existing solutions.

Dr. Matteo Pernechele holds a PhD in Materials Engineering from the University of British Columbia, Canada and a Master's degree in Materials Science from the University of Padua, Italy.

His work spans from scientific research in the general field of solid-state chemistry to industrial projects, especially in the construction and mining sectors. Matteo has 18 years of experience in X-ray diffraction and Rietveld refinement. He has been with Malvern Panalytical since 2018 as an XRD application specialist at the Application Competence Centre in Almelo, The Netherlands.

Dr. Murielle Goubard is Market Development Manager – Building Materials for Malvern Panalytical. She has extensive experience in materials chemistry and worked for 15 years at Solvay Research Centre. She has a deep interest in the cement making process and has been involved in developing applications and solutions for French plants and key European cement companies, while looking to improve efficiency and product quality. With 19 years at Malvern Panalytical, she is now an expert in building materials and is very involved in solutions for green cement plants, circularity and net zero.

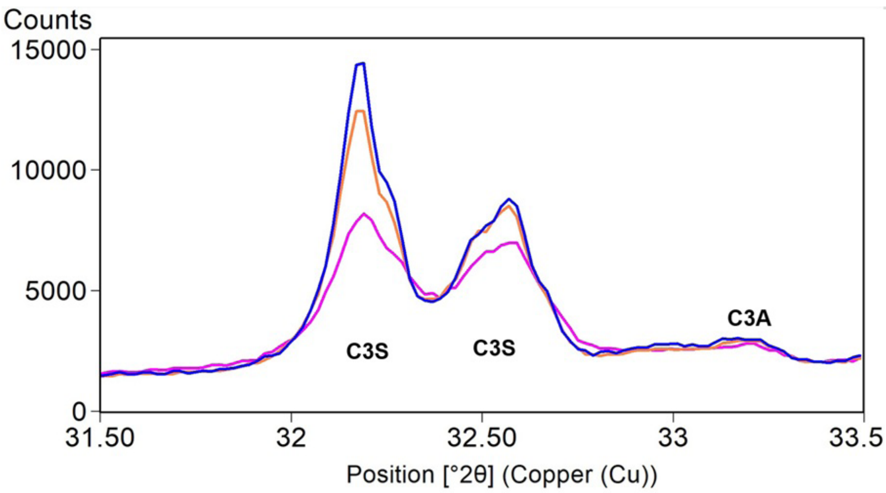


Figure 9. Zoom in XRD patterns of clinker ground with different milling speeds: 750 rpm (pattern with blue), 900 rpm (orange), and 1500 (magenta). The grinding time was constant: 90 sec.

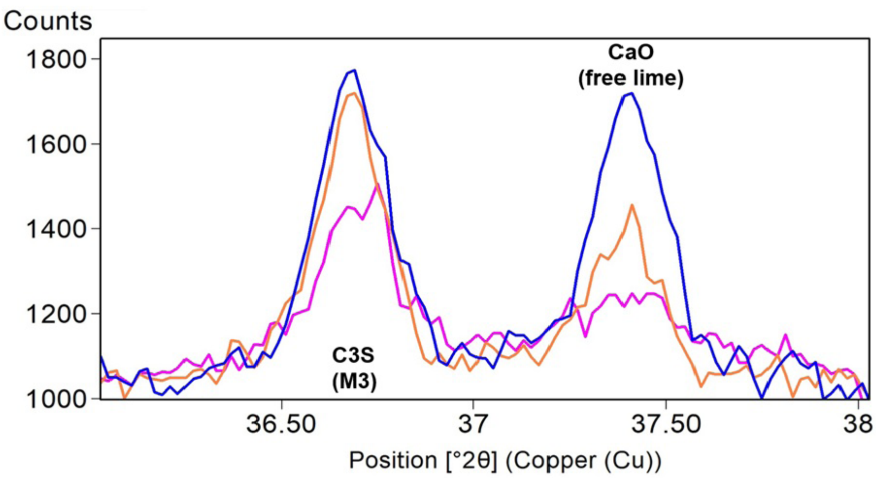


Figure 10. Visible degradation of intensity on the free lime peak as evidenced in XRD patterns of pellets; milling conditions as in Figure 9.