FCT-ACTech
Continuous XRD Analyser

Fact Sheet
Issue #2

April 2003

This document has been prepared to provide a range of information to interested parties about the history, development and current status of FCT-ACTech's Continuous X-ray Diffraction Analyser.

Status

The FCT-ACTech Continuous Mineral Analyser (Figure 1) has been developed in conjunction with CSIRO (Australian Government Research Organisation) and INEL, a French manufacturer of X-ray diffraction equipment. All parties are actively involved in the commercialisation phase of this exciting new technology by FCT-ACTech.

The analyser has been specifically developed to be located in the plant at either the kiln or mill, and to continuously analyse a stream of material flowing through it in order to provide essentially real time analytical results from which automatic control action can be taken. Batch mode analysis is also possible.

The research phase for this on-line analytical equipment involved a spend of almost $10m over a three year period. The results of this research phase included a prototype and a beta test site installation, forming part of the development and evaluation. Production instruments have now been installed at Ash Grove Cement Leamington plant in Utah and at Iluka Resources in Western Australia, and on-line real time continuous mineral analysis for plant control is now a reality.

Figure 1. FCT-ACTech Continuous XRD Analyser

The Technology

Continuous XRD analysis is only made possible by an innovative combination of innovative technologies.

Firstly, a means of presenting a continuous sample stream suitably prepared for X-ray diffraction has been developed. XRD analysis requires an accurately prepared flat bed of material from which diffracted X-rays can be detected. The sample stage is specially designed to prepare and present cement direct from the cement mill (or clinker after milling, or other powdered material) as a flat, continuously moving target bed.

This materials handling system for the XRD sample was devised and developed to allow for a continuous flow of material onto a rotating table that is prepared into a flat bed before passing beneath the X-ray beam.

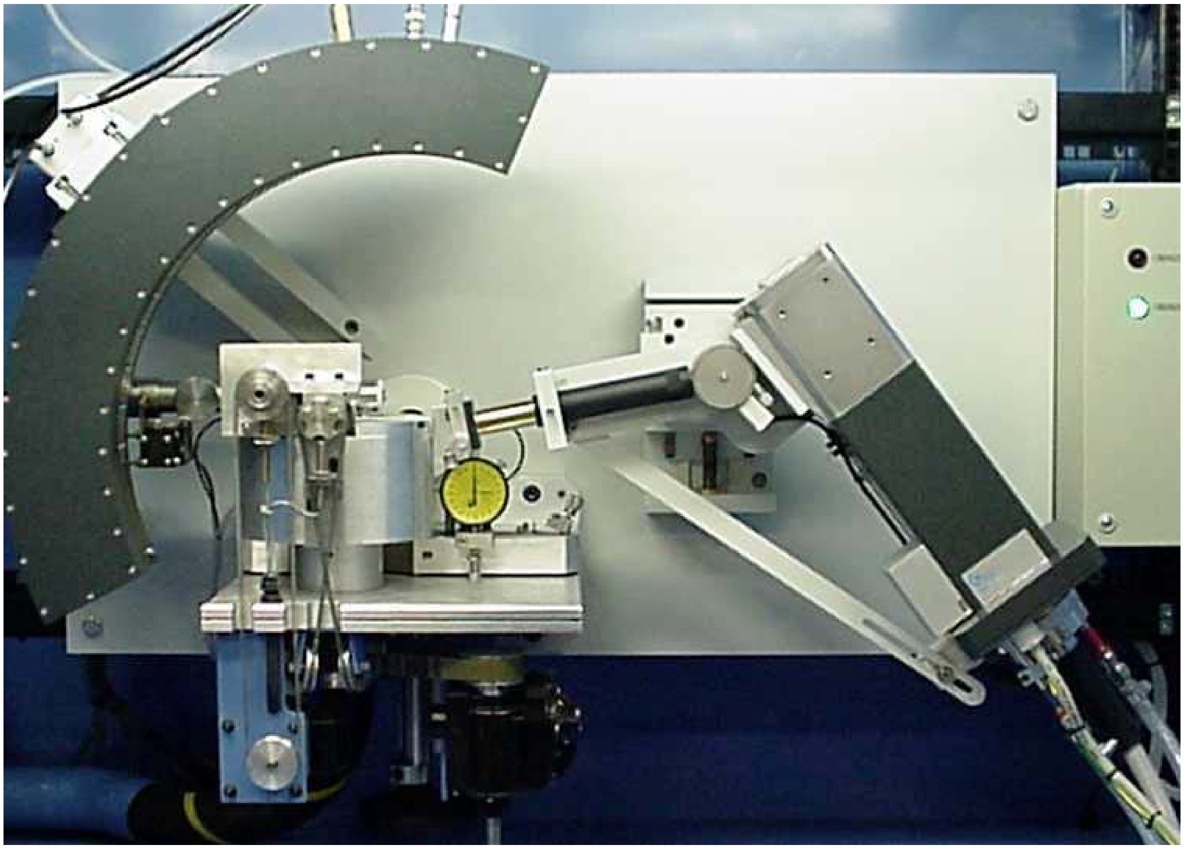


Figure 2 Sample presentation, X-ray tube and Detector.

The analyser uses an X-ray tube and a graphite monochromator (or optional multi-layer mirror) to produce a beam of X-rays at the sample stage. After the analysis zone, the material is continually removed from the rotating table, while new sample is continually added to the table at another point in its rotation. By continuous analysis the requirement for further milling is overcome. For example the analysis is averaged over many orientations because the sample is continuously moving and renewed, and many more individual particles are presented to the X-ray beam, compared to traditional single sample pellets.

Secondly, continuous analysis is made possible through the use of a curved position sensitive detector (PSD) which is able to detect a full range of 120 degrees of 2-theta simultaneously. The PSD produces charge pulses for each diffracted X-ray that are collected from either end of the detector. The position of the detected X-rays is indicated by the arrival times of the charge pulses at either end of the detector curve. The pulse output from the detector is processed into a multi-channel analyser (MCA) via the INEL position detection electronics. The MCA output is then calibrated into 2-theta angles in the software.

The detector is stationary, and therefore more durable and reliable than a scanning goniometer. However, the real advantage in this development is its ability to register a complete diffraction pattern continuously rather than building a diffraction pattern over time from traversing an arc. This means that a complete spectrum of diffracted X-rays is collected relevant to the sample stream flowing through the analyser. This is not possible with a moving goniometer that takes a finite time to scan the diffracted X-ray pattern.

Thirdly, a modified quantitative Rietveld code provides virtually continuous spectral analysis converting the live spectral data to phase composition. Due to the analysis techniques, the instrument is free from requiring standardisation, and will only periodically (annually for example) require check calibration. The instrument has been calibrated for the mineral phases of interest after extensive research and electron microprobe analysis. Using the facilities and expertise of the CSIRO, the calibration of each instrument is preset for each new installation. This is a requirement of the physics of the measurement, not a drawback of the analyser. The calibration accounts for differences in atomic substitution in the various mineral phases, which depend on the raw materials and the process.

The FCT-ACTech Continuous XRD Analyser has been designed to be located in the plant, and not in the laboratory. It has been designed to communicate directly with plant PLC and plant control systems. Its data output can be adjusted easily with software, but in the standard form, all mineral analyses of interest are updated every minute, while averaged values are integrated (typically over a 5 – 10 minute period) to give a smoothed result for control action. In addition, trends are displayed over a nominated time period. Batch mode analysis is also possible.

Furthermore, elemental composition (oxide analyses for example) can be calculated with good accuracy from the mineral composition.

Results in Service

Results from plant trials were published in World Cement in February 2000 and in ZKG in March 2001. Other more recent publications provide more detail on the various aspects of the analyser installation, analysis performance and applications (World Cement February 2002, October 2002 and February 2003).

These studies validate the analytical performance and installed performance of the analyser.

The stability of the analyser over a 15-hour period using a single sample rotating on the sample presentation/preparation stage has been shown to be excellent. The figure below shows the analytical stability for the major clinker phases in a sample of cement.

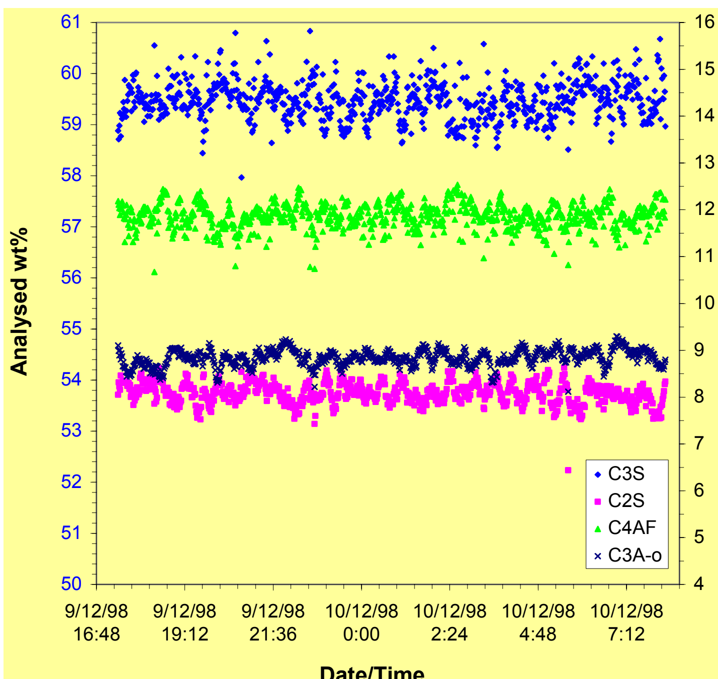


Figure 3. 15-hour repeatability test data, showing the repeatability for a single sample as a standard deviation and relative standard deviation.

The accuracy of analysis is difficult to assess because there are no reliable methods of direct comparison. However, some useful comparisons were devised.

Firstly, elemental or oxide composition was calculated using the measured mineralogy and known elemental composition of the mineral phases and these calculated values compared with XRF analyses that are reasonably accurate.

Figure 4 below shows the very good agreement between the two techniques, indicating high confidence in the mineral analysis of the XRD.

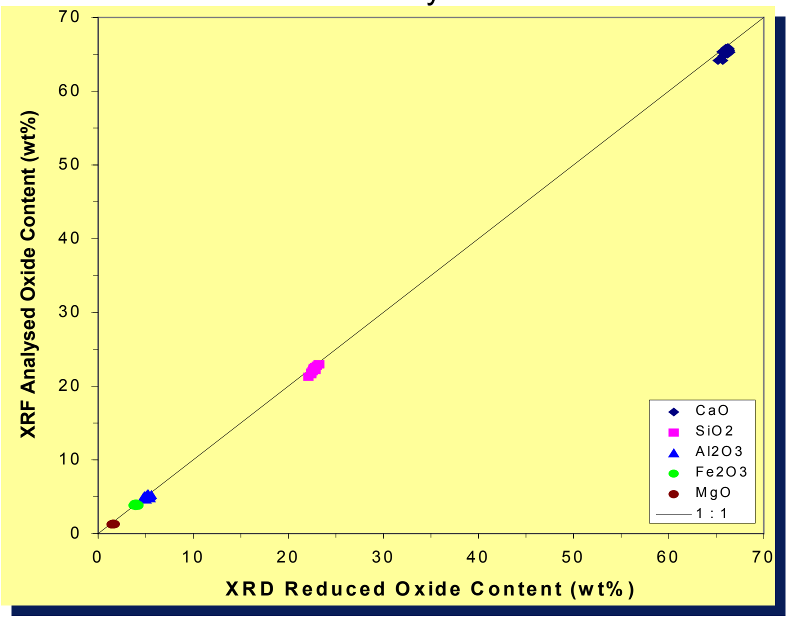


Figure 4. XRD calculated oxide composition vs XRF analysis

Further methods involved weighing known amounts of free lime into clinker and analysing at high temperature to limit free lime hydration. These results are presented in Figure 5 below.

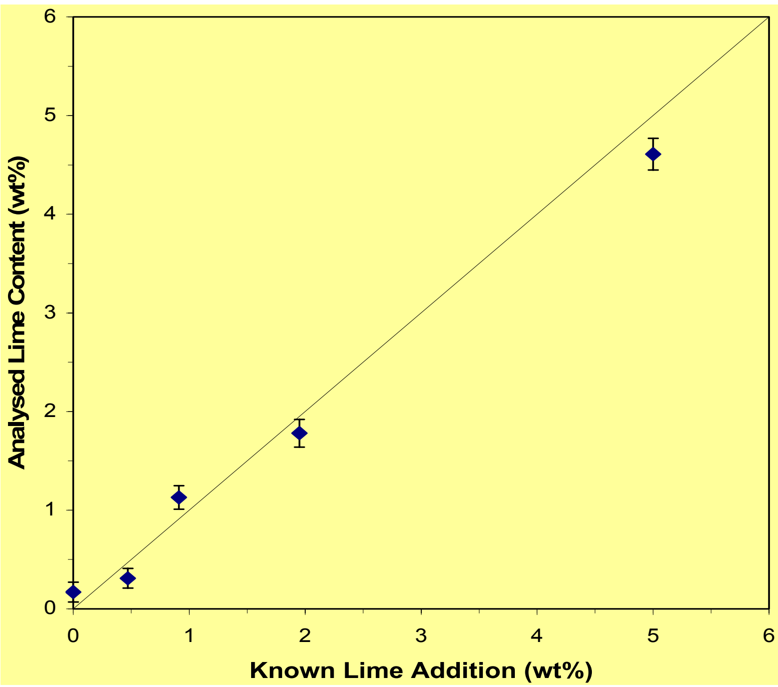


Figure 5. Lime addition weighed vs Lime content analysed by XRD. Agreement is quite good, considering the difficulty in preventing lime hydration during analysis.

Other tests involving addition of limestone of known quantities as well as comparison of XRD analysis with Bogue calculation gave further evidence that the continuous XRD analyser can accurately track changes in the mineral composition of cement and clinker.

This analyser certainly provides a robust and accurate measurement for use in plant control.

Why XRD?

The performance of a cement plant, as well as the cement product to the customer, is governed by mineralogy of the materials and not their chemical composition. The burnability and grindability of materials for example depends on the minerals present, and not the chemical composition as determined by XRF.

The strength development and setting times of the final product is also determined by mineralogy, and not chemical analysis.

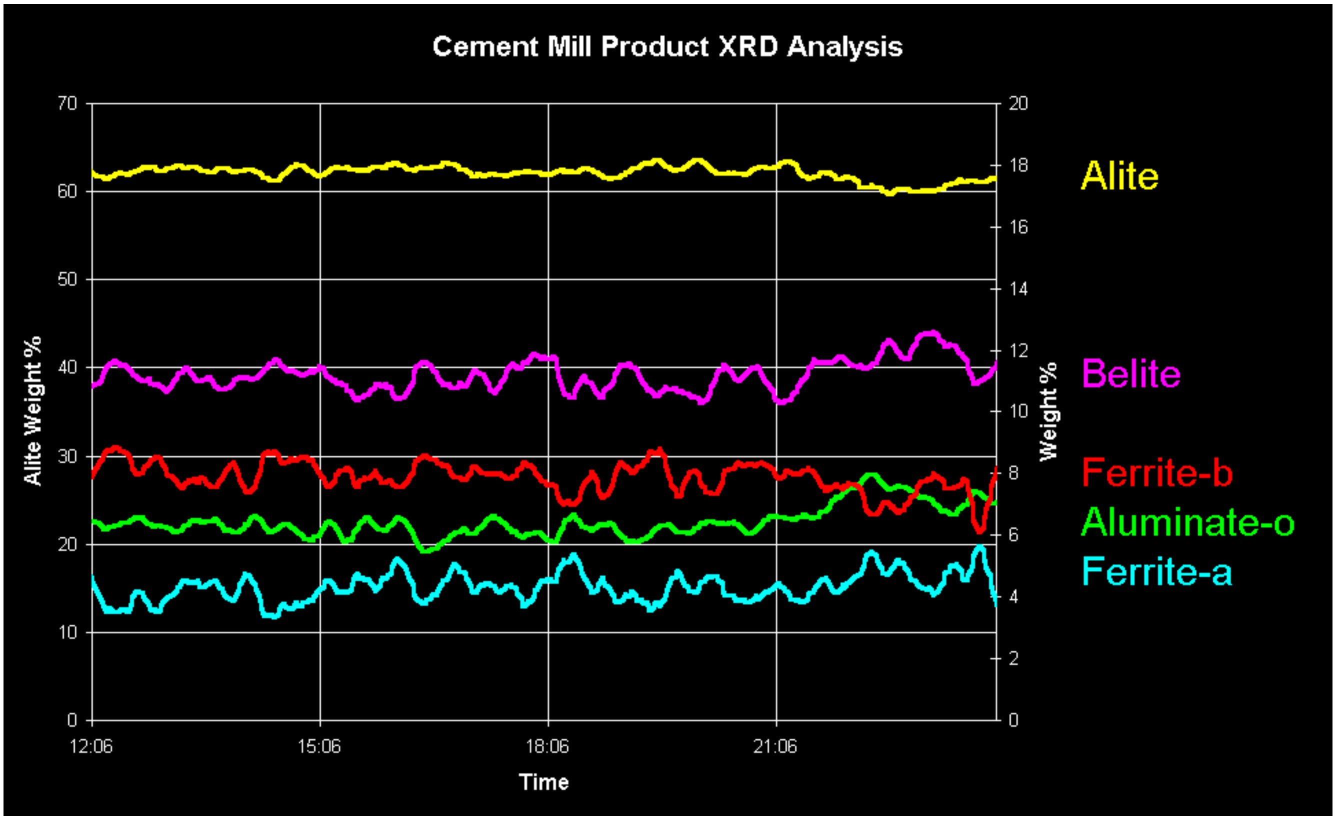
This has long been recognised, and hence the attempt through the Bogue equations to calculate a phase composition from the chemical composition. However, as is also well known, the calculation is theoretical and assumes that equilibrium conditions have been reached in the kiln. The effect of minor elements is also ignored, as are the burning conditions. The difference between the Bogue calculated C3S and C2S and the actual calcium silicate composition can vary enormously. The tri-calcium silicate is often understated by up to 20% or more, and the di-calcium silicate overstated by up to 10%. However, there is no consistency between plants and no consistency on the same plant between different times.

The on-line continuous XRD analyser now provides the means for measuring the mineral composition of cement and clinker directly in real time rather than calculating a theoretical composition periodically from laboratory analysis.

Why Continuous Analysis?

Continuous analysis of a flowing stream of material has several benefits.

Firstly, the amount of sample analysed is very large in comparison to laboratory based techniques. The continuous XRD analyser examines as much material in 10 minutes as a laboratory based automated XRD analyser examines in 48 hours or more. This increases the confidence in the result, and greatly reduces the potential for sampling errors associated with a small sample bead analysed in the laboratory.



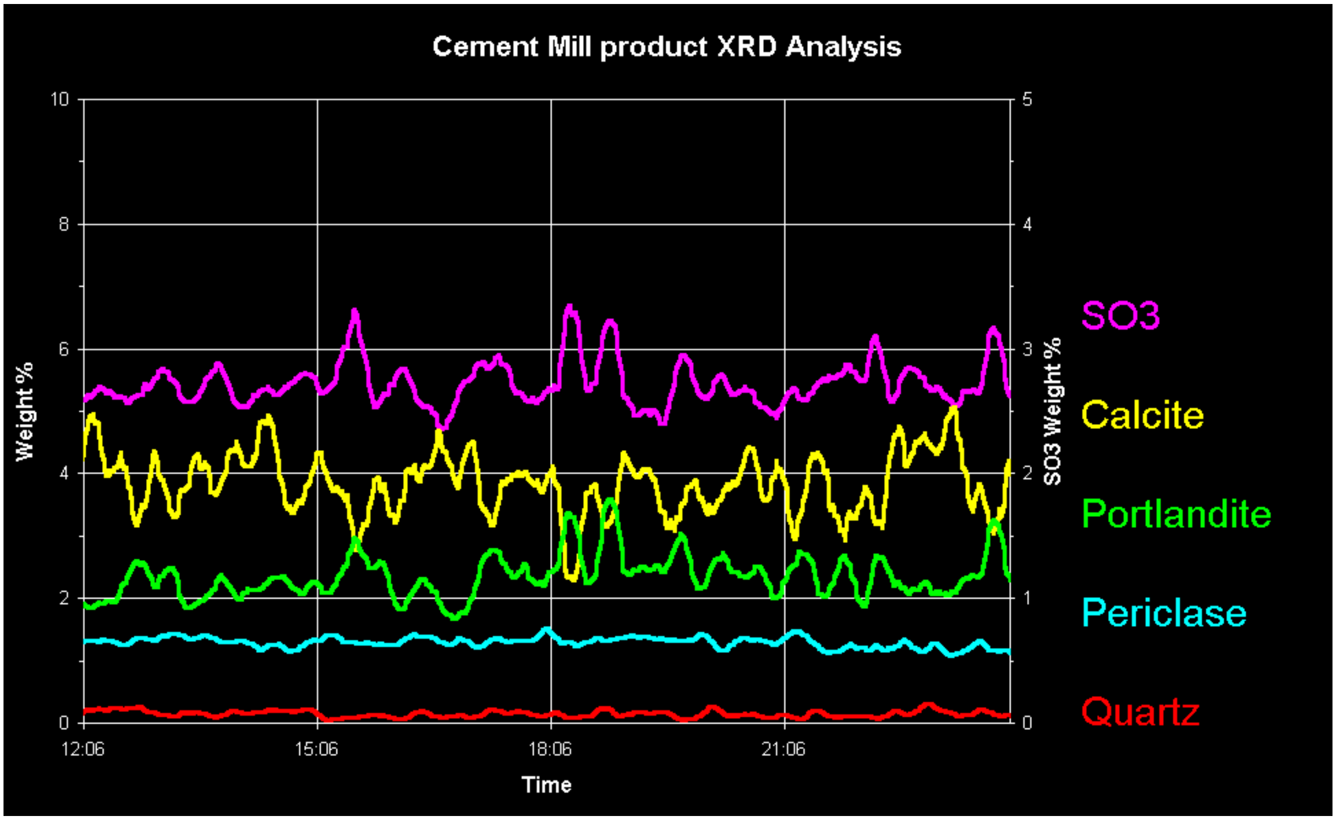
Secondly, the measured result is available in essentially real time as the sample flow passes through the analyser located in the plant. This timely information can be used in an automatic control loop to change kiln burning conditions or cement mill operation for example. The lag time with laboratory based systems is too great for automatic control – particularly if complete phase composition information is required.

Thirdly, the continuous XRD analyser is able to provide a trend of analytical information in the same way that a temperature or pressure can be trended, so that control decisions can be based on trended information rather than single analysis points. This is a large factor in the robustness of a control system using mineralogical information in the control strategy.

What is Analysed?

The continuous XRD analyser accurately and simultaneously measures C_3S, C_2S, C_3A, C_4AF, CaO, and any other minerals of interest in clinker stream ground to 20% +45micron, subject to identification of the mineral, its composition and diffraction spectrum.

Furthermore, identification of alpha, beta and gamma phases of some of the clinker minerals is also possible, leading to the expectation that relationships will be developed between the phases in clinker, the kiln conditions and the performance of the product.



In cement, no further grinding is required for analysis: the final product can be analysed directly from the cement mill. C_3S, C_2S, C_3A, C_4AF, CaO, $Ca(OH)_2$, $CaCO_3$, $CaSO_4.2H_2O$ (gypsum dihydrate), $CaSO_4.{}^1/_2H_2O$ (hemihydrate), $CaSO_4$ (anhydrite) and other Crystalline Minerals as required can be analysed simultaneously as a cement sample stream flows through the continuous analyser.

What benefits?

The on-line continuous XRD analyser opens new doors for optimisation and control of cement manufacture, and will allow automatic control loops for quality control. The benefits are expected to flow from a number of directions, and the following are foreseen as the primary creators of value from this new technology.

1. Plant Optimisation from new knowledge gained

The customer effectively pays $ /Mpa (or $/psi) when buying cement. The cement producer wishes to minimise his production cost in terms of $/MPa (or $/psi).

Cement strength depends on factors such as mineral composition (including pre-hydration, gypsum states, clinker mineralogy, limestone content), mineral reactivity, and cement fineness. However, it is rarely the case that a cement plant knows the inter-relationship between these variables. Although there has been some research into these factors, the volume of information that can be processed is limited with laboratory methods and in any case, the true relationships are probably plant specific.

With on-line continuous monitoring of cement product mineralogy, the relationships between cement product performance and mineralogy will begin to unravel as correlations emerge through statistical analysis.

The first benefit is therefore expected to be an identification of what targets should be established for cement mineralogy to achieve the desired product performance with respect to strength, setting time and other key indicators. As stated earlier, this is not really established in most plants, and production targets are based on many assumptions.

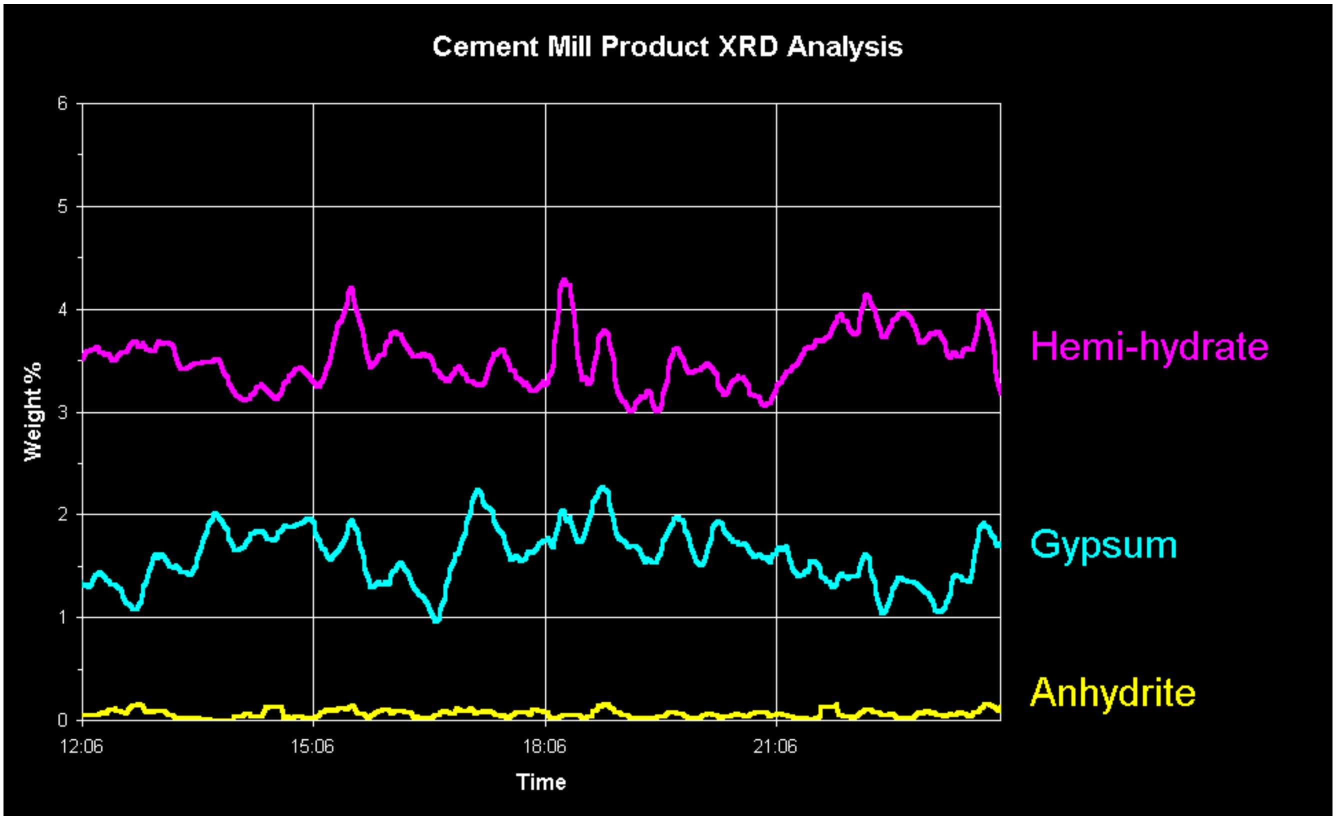
Once the desired product mineralogy has been identified, then this should lead to setting of clinker mineralogy targets, and determination of raw mix chemistry targets and kiln operating conditions to meet the clinker targets.

Once the clinker target has been established, the next stage is to monitor the clinker from the kiln and control the operation to ensure the targets are being maintained. With time, this is likely to include burner control to ensure clinker product of good reactivity as established from mineral phase analysis using XRD.

2. Product Quality Control

Mineralogical monitoring of cement product with the continuous on-line XRD analyser, along with on-line particle size analysis, will allow prediction of cement strength and setting times, and possibly other performance parameters.

If there is a variation in the predicted cement strength development, some action can be taken to mitigate the effect (change in fineness, change in limestone or gypsum content, change of clinker source)



Setting times will be primarily a function of C_3A content and reactivity and gypsum de-hydration states. The continuous XRD analyser measures C_3A content and forms as well as the gypsum hydration states, thus providing the primary data for prediction of cement setting times. A change in predicted values can be counteracted by adjusting cement mill temperatures and therefore gypsum de-hydration.

The XRD analysis also provides on-line real time measurement for control of cement mill weigh feeders for clinker, gypsum and limestone, acting on either mineralogical analysis or the calculated oxide composition.

Prediction, monitoring and control of cement quality at the point of final manufacture is likely to be a significant marketing advantage as well as significantly lowering risk associated with poorly performing product.

3. Reduced Laboratory Testing

On-line real time analysis and control for the cement mill or kiln product will greatly reduce the amount of testing required for either mill weigh feeder control, clinker burning control or quality assurance. In some cases, this may also greatly reduce testing protocols for product accreditation prior to dispatch.

On-Line or Batch Analysis

The FCT-ACTech continuous XRD analyser has been designed for in-plant continuous analysis of a flowing sample stream. In addition though, it can be taken out of continuous mode and into batch mode to analyse a large bulk sample of powder material.

This makes it a versatile instrument that can be used as either an investigative tool or a control device integrated into the process control system.

Installation

Requirements for the total system include:

Extraction of a continuous representative sample of cement or clinker from the process
Clinker grinding mill for clinker sample
Continuous feed of cement or ground clinker sample to the feed hopper of the XRD analyser located in an air conditioned room near the sample point
FCT-ACTech XRD with attached feed and sample disposal hoppers
Specially developed Quantitative Rietveld analysis software for continuous interpretation of diffraction pattern into mineral phase analysis data
Return of disposed sample into process
Self sufficient analysis and data reporting locally at the XRD machine with provision to report data into plant data base and/or operator interface system
PLC interface provision with XRD machine for control of stop/start/sequencing of total system including plant and sampling system

The instrument needs to be supplied with a constant supply of cement or clinker powder and this feed system, air conditioned room and ancillary services can be supplied by FCT-ACTech or by the client.

At the cement mill, a continuous sample of cement, approximately 200grams/minute, should be provided to the sample hopper on the side of the instrument. Level indication in this machine feed hopper signals back to the plant PLC to advise of high or low level. For example the sample could be provided by screw conveyor from an existing or new sampling system.

The instrument should be installed in a sealed, air-conditioned room preferably with split system air conditioning.

The sample is typically extracted from the machine using a vacuum system driven by compressed air. As such, the discharged sample is dispersed in air and needs to be delivered into a location that is under suction from a dust collector or similar.

Clinker should be ground to about raw meal fineness or finer. This could be done with a small continuous mill installed between the cooler and the XRD analyser.

Dimensions

The instrument has been designed as a stand-alone unit, and it can be controlled locally or remotely from the plant control system. The unit is 1.8m high, 1.2m wide and 0.8m deep and weighs approximately 750kg.

Delivery and Project Support

Delivery is typically 26 weeks from placement of order.
Each Continuous XRD analyser is fully tested and calibrated prior to dispatch from our works. Client materials are typically investigated using electron probe and microscopic techniques to identify phases for analysis. FCT-ACTech provides client design support throughout the project implementation for the whole system and support as required for the later performance of the system.

Contact Details

Please contact FCT-ACTech via phone, fax or email for further information.

FCT–ACTech Pty Ltd
20 Stirling Street, Thebarton
South Australia 5031 Australia
Telephone: +61 8 8352 9999
Facsimile: +61 8 8352 9988

FCT Inc
5 Great Valley Parkway
Malvern PA 19355 USA
Telephone: +1 (610) 648 3905
Facsimile: +1 (610) 408 9087

info@fctinternational.com