Plant Optimisation and Control Using Continuous On-line XRD for Mineral Phase Analysis

ZKG Magazine Article *April 2001*

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1 Introduction

In its simplified form cement manufacture involves taking certain raw materials from the earth, mixing them in a ratio that produces a target chemical composition, and processing them mechanically (grinding) and chemically (firing) to produce a final cement product. (see Fig. 1)

Control of this manufacturing process is generally at two levels.

The first is plant and equipment control, where process parameters such as temperatures, pressures and flow rates are controlled to established set points. This has reached the sophistication of automatic control based on expert systems that combine many factors in decision making for adjustments to the plant operating condition.

The second level of control is more fundamental, and is based around the material stream treatment as it flows through the process. This is typically a batch-wise control measure, based on laboratory analysis of material samples periodically taken at various points through the process. This information is used to adjust the set points for the plant and equipment control systems. As examples, chemical analysis of kiln feed material samples is used to adjust raw material proportioning, clinker sample analysis is used to adjust kiln burning conditions and cement sample strength results are used to adjust cement composition or fineness.

There is an anomaly though in that this traditional process control strategy for quality that also affects production costs is based on batch-wise sampling of product streams that provide a historical spot analysis on which to make adjustments for the future operation of a continuous process.
The problems are:

- it is difficult to take a sample representative of the stream
- The stream itself may not be typical of the norm at the time of sampling
- The information used to control the plant is at least several hours and up to 28 days old and may no longer be relevant.

The advent of some on-line analysers in recent years is beginning to address this anomaly of batch-wise control for a continuous process, and is beginning to merge the two levels of plant control into a single system. Typical examples include the on belt raw material analyser that allows virtually real time chemical analysis and control of raw mix composition and on-line PSD analysis for finished cement product.

There can be little doubt that the cement plant of the future will have on-line measurement and control of all major plant parameters, including quality and cost, such that the two levels of control will merge into a single real time system that will continuously optimise plant operation in real time.

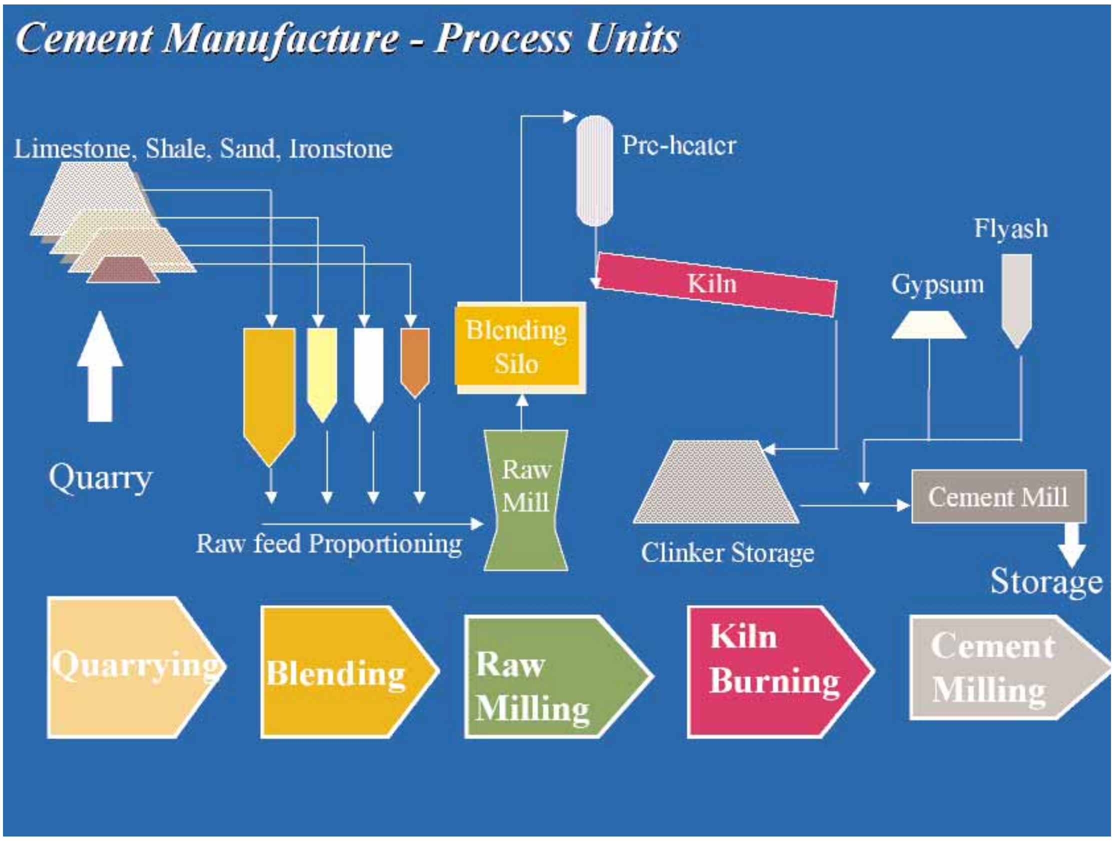

Fig. 1 Cement Manufacturing Process Unit Operations.

2 X-Ray Diffraction

The performance of a cement plant and the cement product itself is governed predominantly by the mineralogy of the materials. Raw material grindability. Kiln feed burnability, clinker grindability, cement setting times and cement strengths are some of the key parameters of cement plant and product performance, and these are all determined by the mineralogy of those materials. However, due to limitations on analytical methods thus far available, chemical analysis has been substituted as the surrogate measure for how these materials will perform.

The use of X-ray diffraction (XRD) for the phase analysis of poly-crystalline materials began development early in the 20th century (Debye and Scherrer, 1916). It is the technique of directing a stream of monochromatic X-rays at a surface and collecting the resulting pattern diffracted from the crystal structure of each phase in the material being analysed. The technique has the unique ability to provide identification and quantification of the crystalline components in a sample of interest, such as cement and clinker. Its potential therefore to provide detailed mineralogical information required for the cement plant operator is apparent. Further details of XRD methodology can be found in Jenkins and Synder (1996) and Bish and Post (1989). Details of the industrial applications of XRD can be found in Chung and Smith (2000), especially Chapter 16 (Madsen and Scarlett, 2000) which relates to the quantitative phase analysis of Portland cement from XRD data.

To this point, XRD has had little use in the cement industry at large except for some investigative and research activities. One of the difficulties has been the analysis of the complicated diffraction patterns as there is a high degree of overlap/interference between the diffraction patterns of the clinker minerals. With development of more powerful computers and increased sophistication of software, these difficulties are being overcome and its relevance to the industry is fast gaining acceptance.

However, for the technique to be useful as a control tool, rapid real time information needs to be available. So far it has been available only as a laboratory based instrument requiring careful sample preparation by fine grinding and pressing into a smooth surface.

FCT-ACTech in conjunction with CSIRO Minerals has succeeded in developing an instrument with unique attributes capable of providing on-line, real-time information on the mineralogy of a sample stream. The new technology has enabled XRD to be taken from the laboratory into the plant where it can now be used to control the process plant ‘on-line’.

This exciting development has been the result of a three-year development program. A prototype has been installed in a cement plant in Australia, producing results that indicate that XRD is a viable, robust technology for cement plant use.

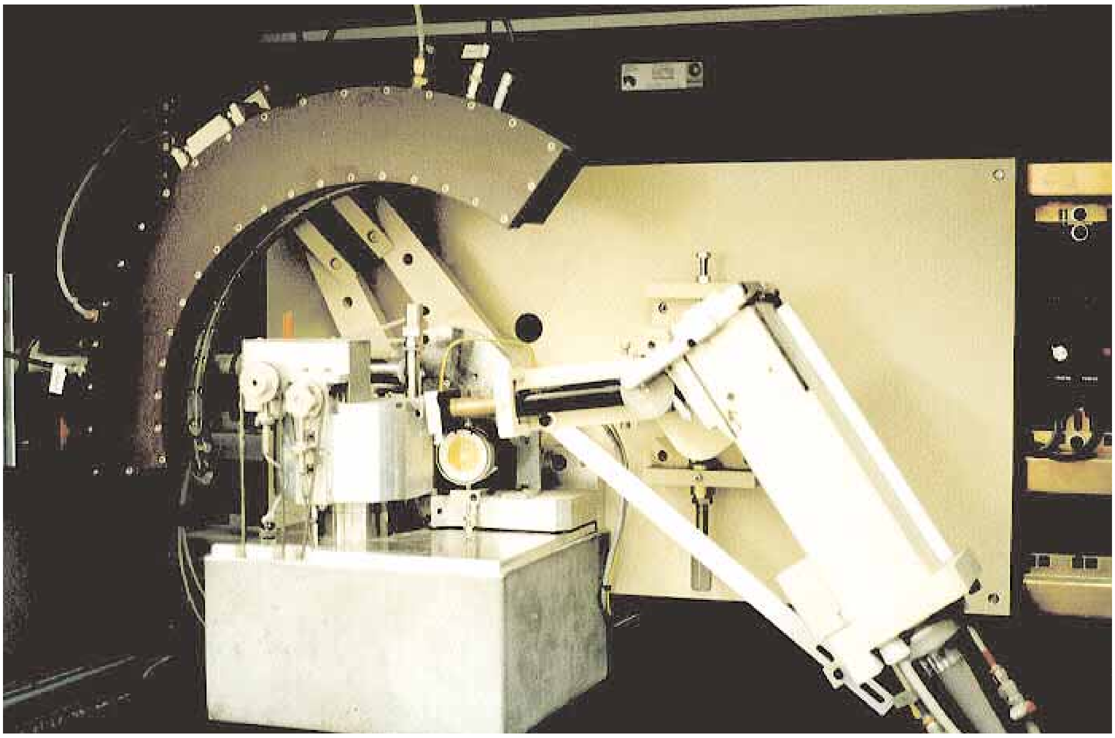

Fig. 2 The On-line X-ray Diffraction Analyser showing, from left to right, the position sensitive detector, the sample presenter, beam conditioning devices and the X-ray tube stand.

3 On-Line XRD Instrument Development

XRD analysers thus far have commonly used a scanning goniometer to sequentially collect the X-Ray diffraction pattern. The process involves preparation of a small sample that is irradiated to produce the diffraction pattern that is collected over 20 – 30 minutes or so before the analysis result is generated. It is a batch analyser taking a finite time to analyse any given sample.

The newly developed and patented instrument shown in Fig. 2 uses a unique combination of:

- (i) simultaneous, rather than sequential, data collection through the use of a position sensitive X-ray detector, or curve detector
- (ii) whole-pattern analysis using the Rietveld method (Rietveld, 1969; Young, 1993), and
- (iii) a sample preparation and presentation system that provides for a continuous flow of material through the analyser.

Some of the benefits of using this approach include (i) very rapid turn-around times for the analyses, and (ii) improved accuracy and lower limits of detection for the phases compared with conventional ‘single-peak’ methods of quantitative XRD analysis .

The instrument provides a continuous readout of all minerals contained in the sample stream. Approximately 600g of sample per minute is analysed in the current configuration. The instrument does not require regular calibration since the analysis software is robust enough to deal with minor variations introduced into the data by the movement of the sample.

An analysis can be provided as frequently as required, and can be updated as frequently as every 15 seconds. For control purposes, a running average over the preceding 5 – 10 minutes is expected to be used. This is software adjustable to suit the application. Such frequent analyses, allows trending of results and provides the ability to control processes ‘on-line’. Furthermore, analysis time is not dependent on the number of minerals being analysed.

The X-rays used in XRD instruments do not penetrate the surface of the powder more than a few microns; hence traditional XRD instruments only analyse a very small sample of the material. Through the use of a continuously flowing sample, the ‘on-line’ XRD analyser is able to examine larger samples of material, thus allowing a greater degree of confidence in the result.

The instrument is also designed such that small batch samples can be introduced to the instrument by ‘interrupting’ the continuous analysis mode and introducing the batch sample (in kilograms rather than milligrams) through a simple hopper. This makes it a versatile instrument in that not only can it be used for on line information and control, but also as an investigative analyser for other material streams including raw materials.

This breakthrough in XRD analysis now means that a continuous sample of material can be fed to the instrument from the cement mill or kiln, enabling ‘on-line’, real time control actions to be taken.

4 XRD Results of Application to Cement Product Stream

The first working instrument has already been installed near a cement mill and is analysing finished product without any additional grinding. It could just as readily be applied to a clinker stream with a clinker grinder in the circuit. However, the application to a cement mill is potentially the most valuable. It has been used to provide the following information.

4.1 Cement/Clinker Phase analysis

The XRD analyser has been shown to give accurate analysis of the major clinker phases (C3S, C2S, C3A and C4AF). This can be used along with other measures to predict the strength of cement and give early warning of developing problems and allow some correction. Changes in the phase composition could be evidence of burning condition problems or raw material changes. Fig. 3 gives the main clinker phase composition for cement product produced from an 80 t/h cement mill over an 8 hour period.

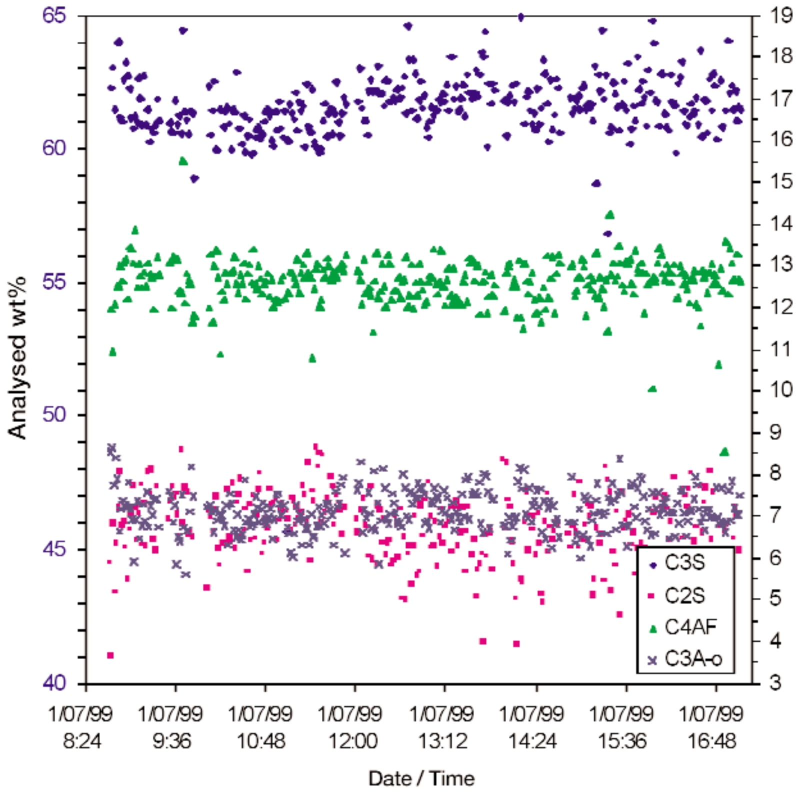

Fig. 3 Phase Composition of Cement Product over an 8 hour Period. The left hand scale refers to the amount of C3S present, while the right hand scale refers to the amount of all other phases.

4.2 Pre-hydration

The analyser also gives an analysis of portlandite (hydrated free lime), giving indication of pre-hydration either in clinker or in the cement mill. This is a factor in prediction of cement strength, and can warn of problems with cement mill water sprays or storage of clinker. Action to mitigate the problem can be taken immediately.

4.3 Setting Times

The ability of the instrument to give accurate analysis of the gypsum hydration states (di-hydrate, hemi-hydrate and anhydrite) has exceeded expectations. This coupled with the C3A content provide the means for controlling setting times by adjusting cement mill temperatures. Fig. 4 shows the gypsum states and percentages in a cement mill product stream over an 8 hour period.

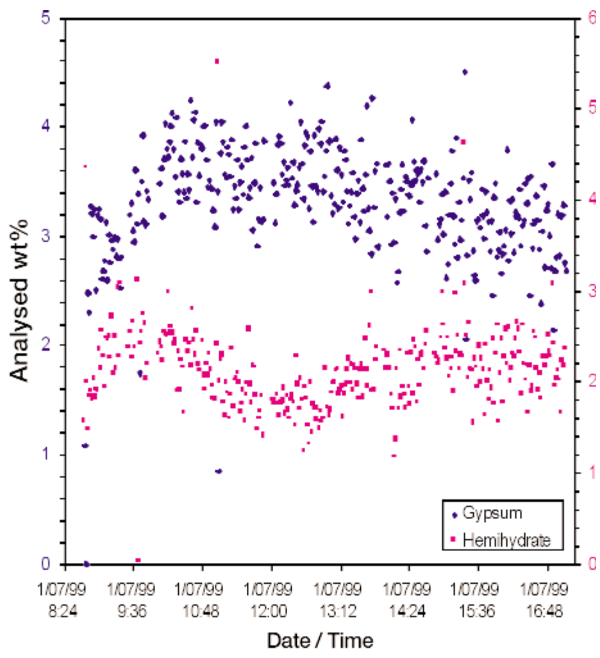

Fig. 4 Gypsum hydration states in Cement Product in an 8 hour Period. The left hand scale refers to the amount of gypsum present, while the right hand scale refers to the amount hemihydrate.

4.4 Mill Feed Proportioning

The analysis of clinker and gypsum minerals, as well as calcite, is accurate enough to provide cement weighfeeder control. The calculated elemental analysis from the phase analysis compares extremely well with XRF analysis, as shown in Fig. 5 and Fig. 6.

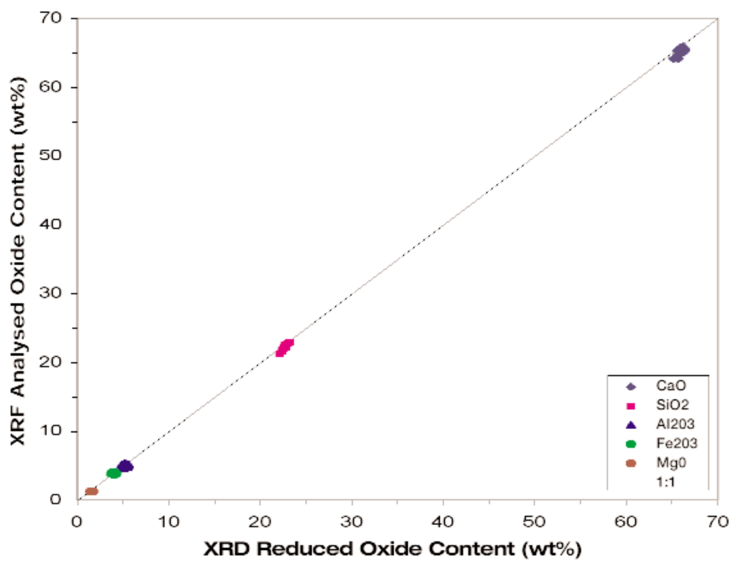

Fig. 5 Chemical Composition calculated from XRD vs XRF analysis. The XRD 'reduced oxide' values are derived using (i) the analysed phase abundances, and (ii) the known compositions of each phase.

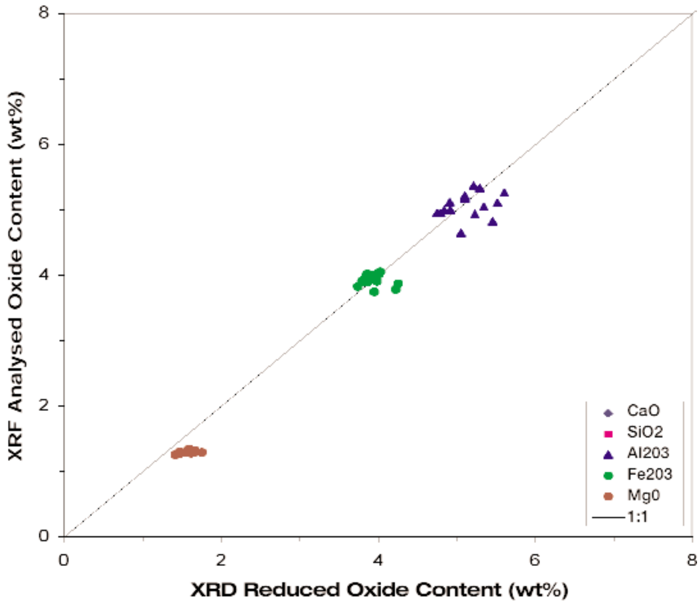

Fig. 6 Chemical Composition calculated from XRD vs XRF analysis (expanded view).

4.5 Free lime

The XRD machine is able to measure both Freelime (CaO) and Portlandite $Ca(OH)_2$. This is important as plant samples of cement and clinker were found to contain mainly portlandite. Freelime (CaO) reacts quickly with any moisture to form Portlandite ($Ca(OH)_2$). Nevertheless, there is a strong linter-relationship between freelime and portlandite enabling control actions to be taken.

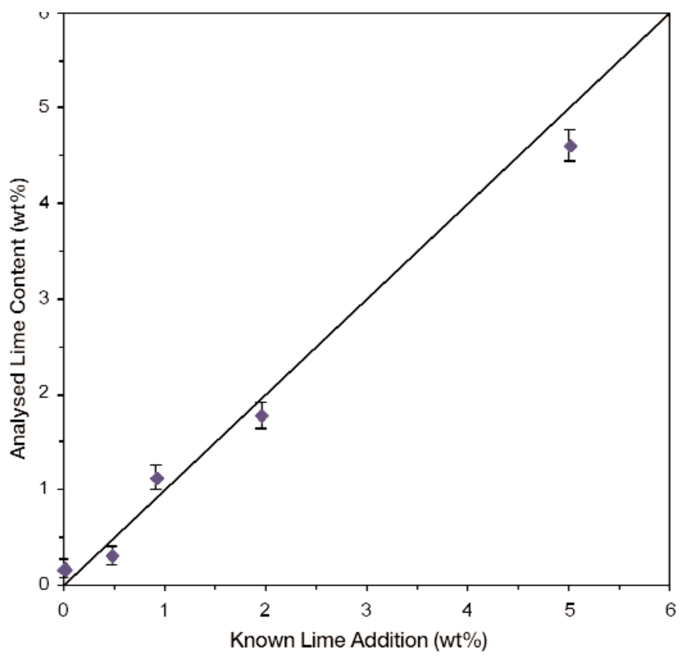

Fig. 7 Free Lime Values derived from XRD Analysis vs the known weight additions.

Figure 7 was derived during laboratory calibration by the artificial addition of lime, ground into a sample of clinker, in order to test the sensitivity of the method for lime analysis. The samples were kept warm to prevent hydration. The XRD machine results for free lime are of sufficient accuracy for plant control.

Analysis of clinker free lime values with XRD is probably the most established use of these instruments so far in the production process. The continuous on-line XRD analyser could be installed on a clinker stream to analyse for clinker minerals and free lime in real time. Alternatively, the analyser could be installed to operate continuously on a cement mill product stream and be used for periodic batch analysis of clinker on the same machine. In either case, results suitable for kiln control would be produced. The benefit of the XRD is that the calcium silicate analysis is also given to indicate whether any free lime is due to underburning or a chemical imbalance.

5 Analytical Stability

During the development phase, the ACTech instrument was tested for long-term stability. Figure 8 and 9 show the stability of the instrument when a ‘batch’ sample was allowed to ‘circulate’ in the instrument for 15 hours producing a result every minute. In this particular case, each data point is derived from the sum of the previous ten data sets. The data shows that a reliable ‘trend’ of cement phases can be produced.

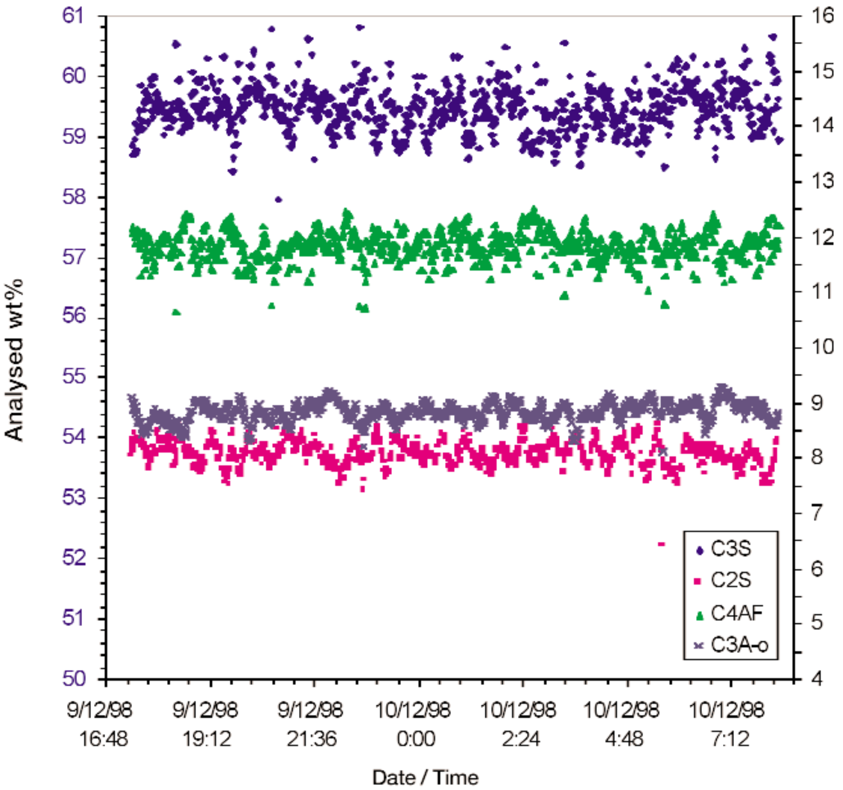

Fig. 8 Analytical Stability over 15 hours analysis of same bulk sample (Clinker phases) . The left hand scale refers to the amount of C3S present, while the right hand scale refers to the amount of all other phases.

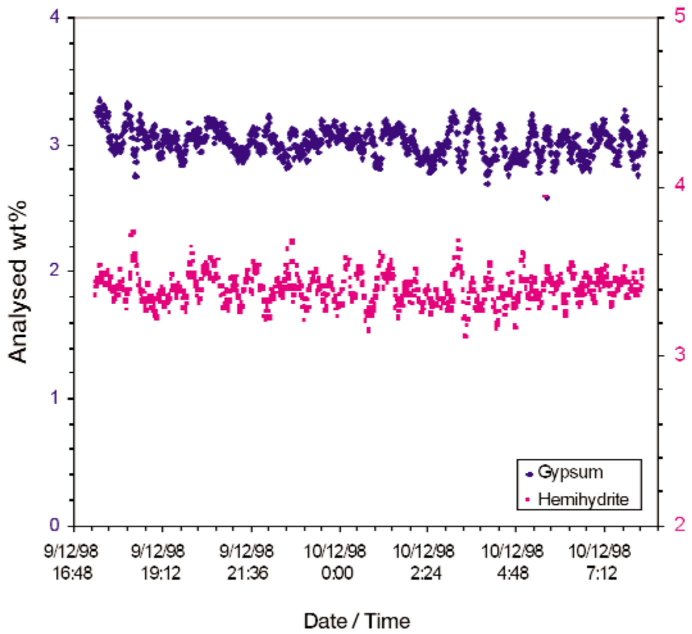

Fig. 9 Analytical Stability over 15 hour analysis of same bulk sample (Gypsum States) The left hand scale refers to the amount of gypsum present, while the right hand scale refers to the amount hemihydrate.

6 Conclusion

The development work and the results achieved with the ACTech instrument 'on-line' at the plant will bring XRD analysis and control to the fore-front of cement mill and clinker kiln operation. It is now possible to measure the phases in finished cement and clinker directly, rather than inferring them from elemental analysis and Bogue calculation. XRD will improve the quality of process control using existing and new control systems. Cement and clinker quality can be controlled 'on-line' using a technique that estimates phase abundances directly rather than inferring it from some other method (e.g. Bogue estimates from XRF analyses).

In summary this instrument:

- Is able to analyse large bulk samples
- Can be a continuous on-line analyser and batch sample analyser
- Can accept up to 600grams per minute of sample
- Produces an updated result every minute or less
- Can analyse clinker phases for strength prediction and correction
- Can analyse gypsum states to predict and control setting times
- Can be used for cement mill raw material weighfeeder control
- Can identify cement pre-hydration (portlandite)
- Can measure free-lime and identify clinker phases for kiln control
- Can identify phases for raw material blending control

This instrument is an exciting development for cement plant operators who have seen the potential of XRD but not yet been able to reap the potential benefits.

Summary

Traditional control of the cement manufacturing process from the point of view of cost, quality and Total Optimisation has been based on batchwise sampling and testing of material streams instigating control action (changing set points) with considerable lag time. These methods have severe limitations to reducing plant variability and achieving optimised operation.

Furthermore, the most significant information for plant and final product performance, the mineralogical composition of raw materials, clinker, cement, gypsum and other materials, has not been available to the plant operator for plant control purposes.

A new development has produced a continuous on-line mineral analyser using

XRD to analyse the various mineral phases present in dry materials (clinker, cement or raw materials) in virtually real time with great accuracy.

The ability to analyse a sample stream continuously for C3S, C2S, C3A, C4AF, Gypsum, hemi-hydrate, anhydrite, limestone, free lime, portlandite or any other phase of interest, has major implications for control of the cement manufacturing process.

The benefits will come from optimising the total plant based on the volume of new information generated, predicting cement performance as it is being produced and controlling to required performance at minimum cost and better quality monitoring and control without associated laboratory costs.

Acknowledgements

The authors wish to thank the staff of the Adelaide Brighton Cement plant at Birkenhead for their assistance and advice during the plant installation and testing of the analyser.

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