A NEW ON-STREAM XRD TECHNOLOGY FOR MEASUREMENT AND CONTROL OF GYPSUM DE-HYDRATION/SETTING TIMES.

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Introduction

The quality of a supplier's cement is determined by key performance parameters such as setting time and strength, so it is imperative that these are controlled carefully. This article describes how cement producers are using the benefits of continuous on-stream X-ray diffraction analysis of cement to monitor and control gypsum dehydration in the cement finish mill. Better control of gypsum dehydration leads to better control over cement setting time and strength development. These producers are providing themselves with a marketing edge over their competitors.

Dynamic Gypsum States

It is well known that a key factor in the setting time of cement is the hydration of calcium sulphate ($CaSO_4$, see Table 1, Ref (1)). In Portland cement manufacture, gypsum (or gypsum plus anhydrite) is interground with the clinker to produce the finished cement. Some form of $CaSO_4$ is required to control the setting time, since without it the ground clinker would flash set. However, the changes that occur when grinding gypsum are not just physical, since the grinding process adds energy, which can elevate temperatures to levels that drive off bound moisture. At temperatures above about 105^{o}C partial de-hydration of gypsum produces hemi-hydrate. Anhydrite will begin to form at temperatures above about 170^{o}C. Natural forms of anhydrite are available (as gypsite) and these may be added to Portland cement clinker to provide generally up to around 50% of the $CaSO_4$. Continuous on-stream X-ray diffraction analysis provides the only means for directly measuring these components of the cement in real-time.

Mineral	Formula	Properties
Gypsum	$CaSO_4.2H_2O$	The main naturally occurring form of calcium sulphate, as dihyrate. Moderate solubility.
Hemihydrate	$CaSO_4.½\ H_2O$	"Plaster of Paris". Normally formed from gypsum at temperatures above about 105^{o}C. Highly soluble. May be available in a low solubility natural form.
Anhydrite	$CaSO_4$	Forms from gypsum or hemi-hydrate at temperatures above about 170^{o}C. Highly soluble in this form.

Table 1 Forms of calcium sulphate.

Known benefits of gypsum dehydration include improved final cement strengths and better flowability of cement in storage silos. These benefits must be weighed against the possibility of false set that arises in the case of too much hemi-hydrate, while the setting times may become extended in the case of too much gypsum.

Actually controlling the hydration of gypsum in the finish mill is a balance between a number of factors. The traditional method of controlling the gypsum dehydration is to control the temperature of the product as it leaves the mill. Mill exit temperature may be controlled by internal water sprays and/or water cooling of the mill shell. However this type of control is far from sufficient to control gypsum dehydration, since the rate of dehydration of gypsum increases significantly as temperature increases above the threshold. Besides the exit temperature, there are other factors that need to be taken into account, such as clinker temperature at the mill inlet, feedrates at the various points in the grinding circuit, clinker grindability, clinker free lime content and the temperature and humidity of the air sweeping through the mill.

Installations

Cement plants are nowadays taking a proactive approach to ensuring the quality of their product (Refs (2),(3)). This can be achieved using continuous on-stream X-ray diffraction analysis of their cement product as it leaves the finish mill (Figure 1), rather than waiting for the laborious and time consuming results of physical testing. By measuring cement minerals such as calcium aluminate percentage and forms, alkali sulphates and the degree of $CaSO_4$ de-hydration in the final product cement, the cement setting times can be predicted and then controlled. Producers can then ensure that their customers reap the benefits of a more uniform product.

Figure 1 A Continuous On-Stream XRD Analyser installed at the finish mill.

This type of quality control at the finish mill has only recently become available in the form of continuous on-stream X-ray diffraction analysis of the product stream. FCT-ACTech produces the only X-ray diffraction analyser that performs continuous mineralogical analysis of cement (or any other powder, eg. ground clinker or raw meal) as it is extracted continuously from a process stream. This is a major step forward for process control using cement mineralogy, rather than chemistry, that has been achieved through a collaboration between FCT-ACTech and the premier Australian government research organisation, the CSIRO[1]. The FCT-ACTech Continuous XRD Analyser is shown in Fig 2, and Fig 3 shows schematically how the sample for analysis may be extracted from the product stream and passed through the analyser, before being pnuematically returned to a dust collection point.

[1] Commonwealth Scientific and Industrial Research Organisation (Division of Minerals)

Figure 2 FCT-ACTech's Continuous XRD Analyser

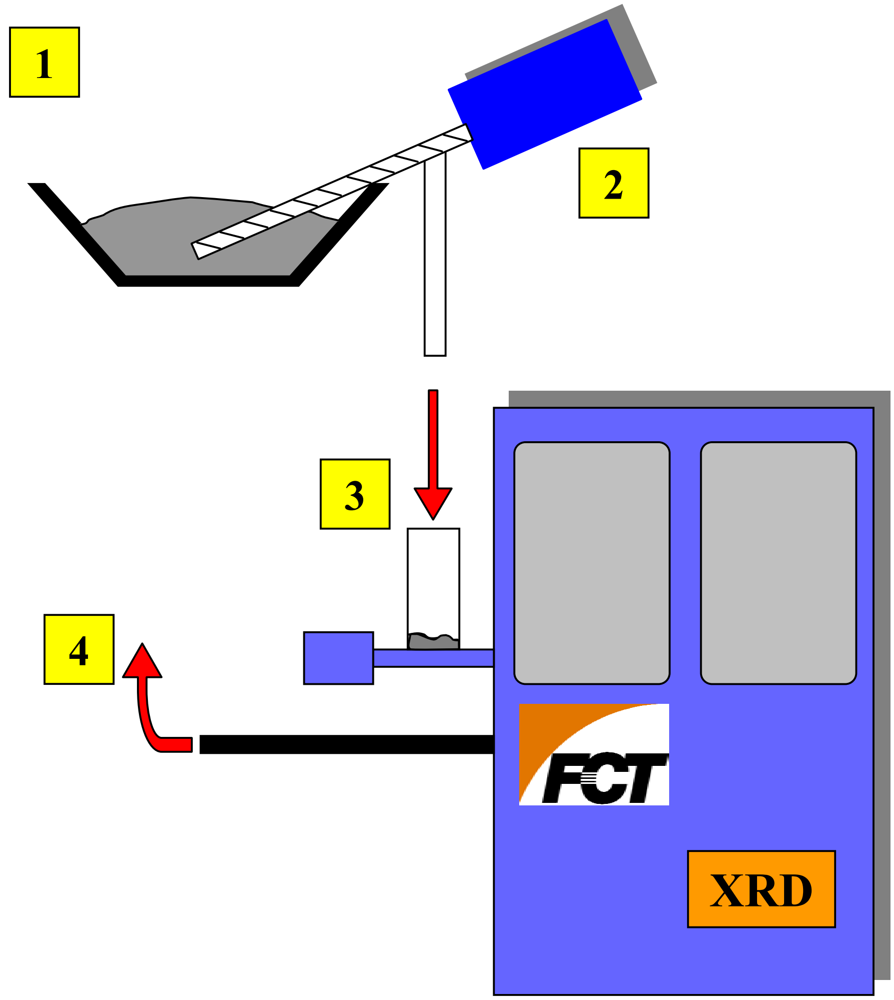

Figure 3 Schematic of continuous sample extraction from a cement product conveyor (1) by a sample auger (2), which delivers a flowing stream of cement through the XRD (3), followed by continuous pneumatic return of the analysed sample to a nearby dust collector (4).

State of the art analysis

By tapping into many years of crystallography experience at the CSIRO Division of Minerals, FCT-ACTech has been able to coordinate the development of continuous on-stream X-ray diffraction analysis for the cement manufacturing process. This development takes X-ray diffraction out of the laboratory and brings it to the process, allowing positive control action to be taken using the analysis results. Using a patented wide-angle detector a complete diffraction pattern is collected simultaneously over all angles. Naturally, the diffraction pattern analysis software uses a fundamental parameter Rietveld analysis, which is the best possible analysis technique. In addition, each analyser is provided with a set of customised input parameters based on a selective examination of the plant cement, clinker or raw meal, to further optimise the analysis accuracy.

Using Rietveld analysis it is straightforward to automate the direct measurement of hydration of $CaSO_4$. Indeed the Rietveld technique is a comprehensive standardless method, so each analysis routinely provides a complete breakdown of all of the mineral components of the material, as shown in Figure 4. Also, notice that the analyser reports chemistry, shown in the right hand column in the figure. This is made possible by determining the chemical composition of each of the mineral phases (alites, belites, etc) in advance using microscopic analysis techniques such as electron probe analysis. These predetermined compositions are used along with the mineral phase analysis to calculate the chemistry corresponding to each analysis. The calculated chemistry can be used to good effect. For example, the SO_3 analysis can be used to control the gypsum feeder settings to ensure that the SO_3 level is maintained at the correct setpoint for each type of cement produced.

Minerals		Elements	
Alite	54.81	SiO2	20.89
Belite-b	15.79	Al2O3	4.76
Belite-g	2.56	Fe2O3	2.70
Ferrite	11.04	CaO	63.59
Aluminate-o	2.62	MgO	2.47
Aluminate-c	2.50	TiO2	0.26
Lime	1.40	SO3	3.07
Portlandite	1.12	Na2O	0.12
Gypsum	4.77	K2O	0.45
Hemihydrate	0.85	P2O5	0.12
Anhydrite	0.27	Loss	1.43
Calcite	0.25		
Quartz	0.46		
Periclase	1.19		
Arcanite	0.29		

Figure 4 Composition output from the analyser's Rietveld analysis software

The accuracy of the Rietveld analysis has been proven in many tests. As an example, the method's ability to measure hemi-hydrate is demonstrated in the simple results presented in Fig 5. Here the test was to dose a pre-ground clinker sample with a manufactured hemi-hydrate sample (produced by heating ground gypsum to 130 degrees in an oven.) Several samples where constructed by combining known weights of clinker and hemi-hydrate. The analysis by XRD clearly agrees with the results expected from the scale measurements, showing the accuracy of the XRD response to varying levels of hemi-hydrate.

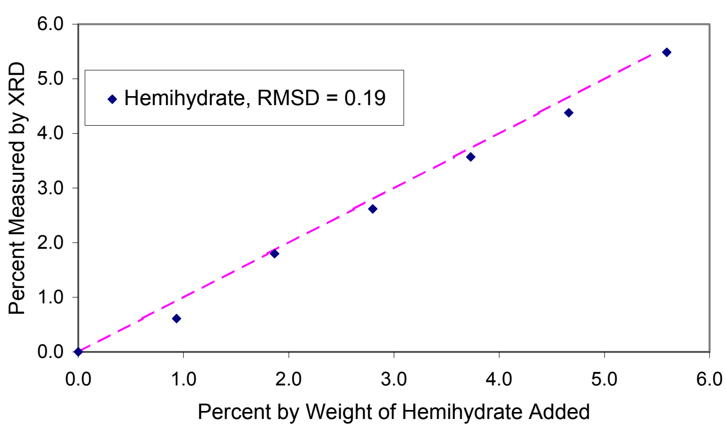

Figure 5 Hemi-hydrate measured by the continuous on-stream XRD analyser.

Continuous On-Stream X-ray Diffraction Analysis

These laboratory results are of academic interest, but the true value of continuous on-stream XRD analysis is in the potential for process control. As installed, the FCT-ACTech analyser monitors the cement by examining a continuous sub-sample of the material from the product stream. The sample is extracted from the product by an auger or other sampler and dropped directly into the XRD feedhopper. From the feedhopper the sample is passed to FCT-ACTech's unique sample presentation system, which presents a moving flat bed of cement to the X-ray beam. The diffracted X-ray pattern is collected over 0 to 120 degrees simultaneously by a position sensitive detector. A Rietveld analysis technique is used to analyse the resulting diffraction pattern, providing an analysis of the moving stream once every minute, as shown in Figure 6.

Once the cement has passed the X-ray beam the sample is continuously removed from the sample presentation system and conveyed pneumatically back to the process. Several kg/hr of cement may be analysed in this manner, greatly reducing sampling error. In addition the moving stream of cement passing the X-ray beam reduces errors particular to X-ray diffraction analysis, such as preferred orientation. The trended analysis results give a further assurance of quality, along with increased confidence in the results through their inherent self-consistency throughout the trends. In other words, rather than having to ask why an outlier has appeared in an analysis data set, with continuous analysis it is possible to view the trends and gain an understanding of how deviations from the ideal have developed over time. Naturally all analysis results are communicated directly to the plant PLC system (and also displayed and stored locally on the analysis computer.)

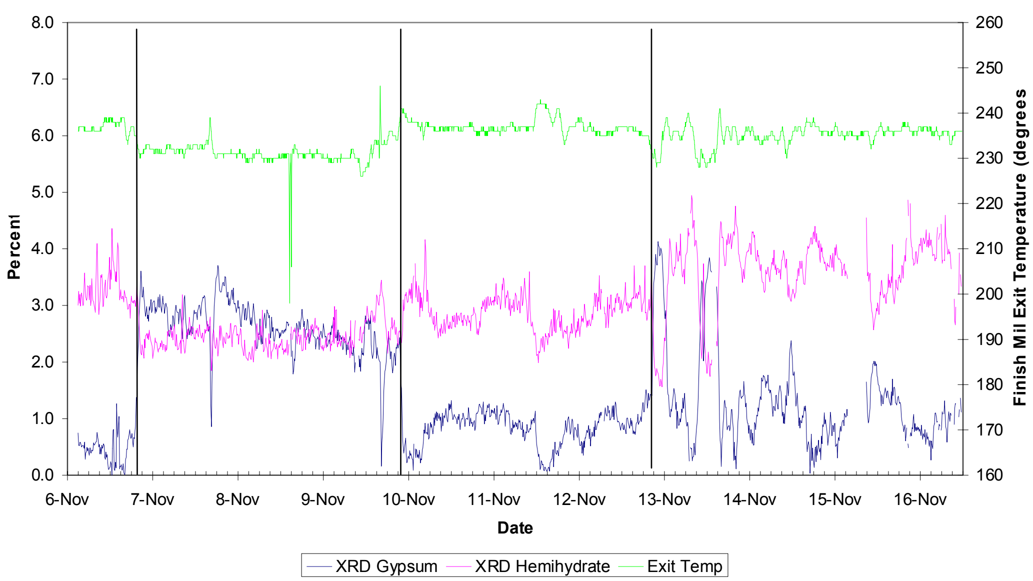

Figure 6 Live gypsum state trends from cement mill product stream using continuous on-stream XRD.

In the case of continuous analysis of the cement mill product, at least two features are immediately apparent. Firstly the behavior of the $CaSO_4$ hydration states is broadly as expected, such that when the temperature in the mill increases, there are corresponding increases in hemi-hydrate (compared to dihydrate) and vice versa. However with the traditional methods, while the general behavior or tendency is as expected, the actual achieved ratio of gypsum to hemi-hydrate is not always as expected, and not necessarily under control. The reasons for this are varied, and include factors such as the clinker temperature at the mill inlet, feed rates into the mill, clinker grindability, the temperature and humidity of the air sweeping through the mill and the return rate from the separator.

In one clear case, shown in Fig 7, the ratio of hemi-hydrate to gypsum was seen to swing from about 1 to about 4, even though the mill exit temperature was controlled to better than one degree. This was subsequently found to have happened for the simple reason that the temperature of the clinker entering the mill increased. In this case the intention was to hold the ratio of gypsum to hemi-hydrate constant by keeping the mill exit temperature constant, but at around 19:00 on 25 February 2002 this control strategy was seen to fail. It was at this time that the temperature of the clinker at the mill inlet started to increase. Of course this information is not available in real-time without continuous on-stream X-ray diffraction analysis, so it is clear that many plants are routinely producing cement with wide variations in the ratio of gypsum to hemi-hydrate, and struggling to live with the problems that this can create.

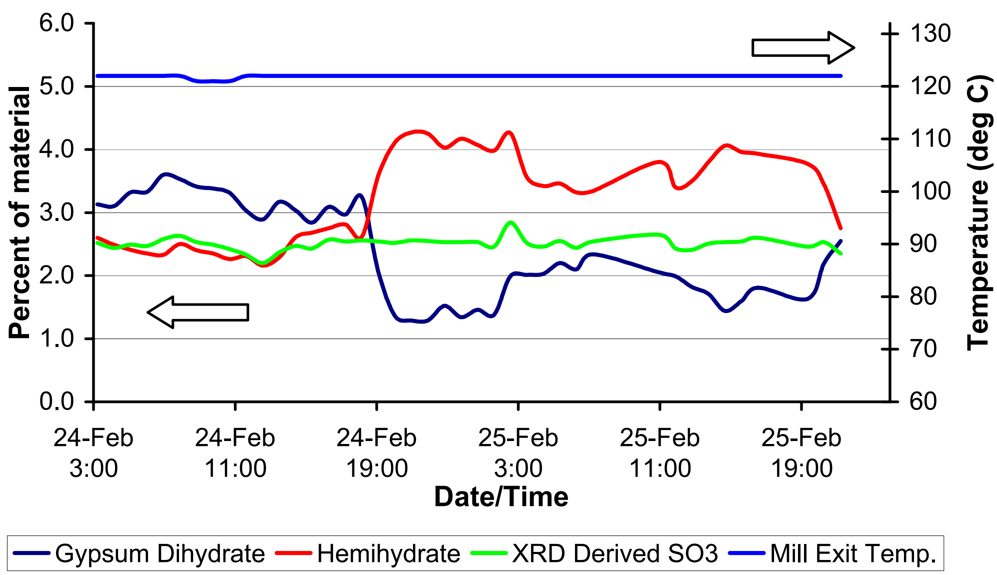

Figure 7 Gypsum hydration in real-time, by continuous analysis of the finish mill product

Setting Time Prediction

The analytical information from the continuous on-stream XRD analysers in operation is being processed to determine the correlations between setting times and mineralogical composition. Setting time will depend on a number of mineralogical parameters, including gypsum hydration states, free lime, calcium aluminate content and forms, alkali sulphates and calcium silicate forms. All of these can be determined by the Continuous on-stream XRD analyser in real time, paving the way for prediction and control of this often critical quality parameter.

Even with the limited data available to date from this new technology, the likely success of this statistical approach is apparent, with good agreement between actual and calculated setting times possible. Figure 8 shows some calculated setting times compared to the laboratory test results on one such data set.

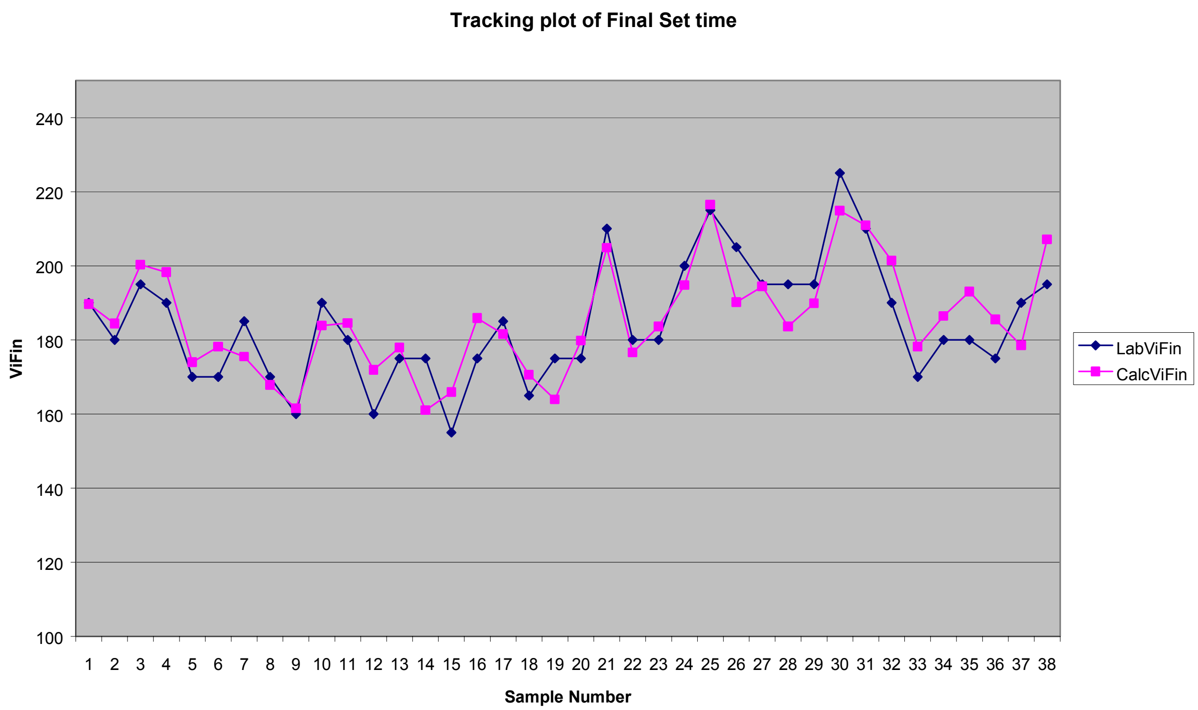

Fig 8 Calculated setting times from mill product using continuous XRD vs actual setting times as tested in the physical laboratory.

Once this quality variable can be predicted, then of course it can be controlled. The main short term control measure will be to vary the mill exit temperature of the product cement to control the gypsum de-hydration and hence the setting times. Longer term measures may include raw mix design, kiln operation and clinker free lime targets.

Conclusion

Many plants are capable of producing high quality product, but in today's highly competitive marketplace only the best plants will maintain market share. That is why all plants expend so much effort in quality control. However even the best quality control systems have their weaknesses, and batch testing for physical parameters such as setting time is not really adequate, especially when considering working hour constraints and testing delays. Consumer confidence can be powerfully affected by "quality excursions", and these happen in real time. Even a single bad experience is always remembered long after the event, so it would be unwise to only consider production cost benefits in a capital justification for quality control equipment. In this light it is easy to see why a company would chose Continuous On-Stream XRD Analysis as a tool to provide online quality control, which takes them a step closer to total quality management.

References

(1) Bellotto, M and Signes-Frehel, M, 'The Role of Powder X-ray Diffraction in the Cement Industry', European Powder Diffraction, Materials Science Forum, Vols 278-281, 1998
(2) Manias, C, Storer, P and Retallack, D, 'Proactive Not Reactive', *World Cement*, Feb. 2002.
(3) Manias, C, Retallack, D and Madsen, I, 'XRD for On-line Analysis and Control', *World Cement*, Feb 2000.