EXPERIENCES WITH CONTINUOUS ON-STREAM XRD AT THE ASH GROVE LEAMINGTON PLANT

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Abstract

An on-stream X-ray diffraction analyzer has been monitoring the finished cement at the Ash Grove Leamington plant since October 2001. The complete mineralogical composition of the cement is provided by continuous analysis of cement extracted from the product conveyor with results presented as trends. The analyzer has been operating well, showing consistent agreement with traditional forms of analysis such as XRF and free lime titration. Trends of the XRD analysis have been used to identify contamination of the gypsum additive, and variation of the gypsum hydration states can be clearly seen. The XRD analysis has been used to control the rate of gypsum addition to the finish mill, starting from mid-2002. Further control loops are expected as relationships between mineralogy, strength and setting times evolve. The continuous XRD has provided plant personnel with a dynamic real time trend window into the quality of their cement production process.

Introduction

In recent years the application of continuous analysis to cement production and quality control has increased significantly. Many plants have one or more forms of on-stream analysis and in the areas of stockpile and raw mix control the use of continuous analysis is now routine. In cement and clinker production however, the use of continuous analysis is less common. Figure 1 shows the continuous XRD that is installed at the Leamington plant. At Ash Grove we decided some time ago that on-stream instrumentation is the ideal way of providing quality control. The potential for significant cost savings through optimized plant operation and from labor reduction provides an attractive incentive for this approach.

In this presentation we discuss our operational experiences using continuous XRD analysis of the cement mill product at the Leamington plant of Ash Grove Cement. Overall this has been a positive experience, with an instrument that is relatively trouble free, easy to work with and reliable. The analyzer gives reproducible and consistent results, which compare favorably with alternate means of analysis, such as XRF and free lime titration. Note however that the XRD is giving a direct measure of the mineralogical composition of the cement, and in this case the measured mineralogy can be different from the mineralogy as determined by traditional methods, such as by using Bogue formulas.

Production shift operators recognize that the instrument is able to provide them with valuable feedback on the process, which is more timely than the traditional composite samples. In addition the continuous trends provide information that may otherwise be masked by a composite analysis. The XRD provides the operators with a continuous real time source of information about the process that they are trying to control.

Continuous analysis of the finish mill product has been operating since the XRD analyzer was installed in October 2001. After a period of evaluation the control of the gypsum weighfeeder was switched from the four hourly laboratory XRF SO_3 analysis to the XRD analyzer. The XRD analyzer produces an analysis every minute, and can smooth the previous ten minutes of collected data for control action. A rolling average of the XRD derived SO_3 result is now being used to adjust the gypsum feedrate.

Figure 1. Continuous XRD Analyser

<u>XRD applied to cement</u>

XRD as an analysis technique has great value when applied to cement. The primary reason for this is that XRD is able to directly measure the mineralogy of the cement, and it is the mineralogy, along with the particle size, that determines the properties of the cement. Traditionally the control and monitoring of materials on a cement plant has been done using the cement and raw material chemistry, and the mineralogy has been implied using the Bogue potential formulas. These Bogue formulas assume that all of the chemicals that make up the cement have been processed under ideal equilibrium conditions. In practice the conditions are rarely ideal and for this reason an XRD can provide invaluable information to cement plant operators about the true operation of the process. In addition XRD is able to identify particular mineral species that may not be isolated by an XRF measurement alone. These minerals include free lime (CaO) that results from the pyro-processing, hydrated free lime in the form of portlandite, contaminants such as calcite in the gypsum feed and the different amounts of gypsum, hemihydrate and anhydrite that are formed in the cement mill from the gypsum feed.

Since cement is a complex of minerals it seems obvious that XRD is an ideal tool for monitoring composition. However it is only in recent years that the software and hardware have reached a point where the full complement of minerals can be routinely determined from a measured X-ray diffraction pattern. In addition the hardware for measuring cement diffraction patterns in a continuous manner has only recently been developed. The necessary hardware and software for the diffraction analysis will be described below, but first let’s look at how the cement is presented for analysis.

Figure 2. XRD room next to mill building at Leamington

The installation of the XRD is in a small building next to the cement mill, as shown in Figure 2. The building houses the XRD, and in a side room there is an air conditioner and a chiller to provide cooling water for the X-ray tube. The cement is extracted directly from the finished cement conveyor, which runs in the large pipe above the room, across to the dispatch silos.

Figure 3 shows how the cement is extracted from the product stream. A single conveyor receives all of the production cement, and it is used to transport the cement to the dispatch silos, which are located above a truck and rail load-out about 500 yards from the finish mill. An auger that is positioned in the cement flow is used to extract a cement sample from the conveyor belt. The cement sampled by this auger then drops down to the XRD feedhopper via a two inch diameter pipe. The auger supplies cement at a rate that maintains a cover of cement over a level sensor in the XRD feedhopper.

The XRD feedhopper is mounted directly above an internal feedscrew, which continuously feeds the cement into the analyzer sample presentation stage. Cement drops about an inch from the exit of the feedscrew, down onto a sample turntable, with any excess dropping into the bottom of the sample stage. This excess is extracted from the XRD by a pneumatic venturi eductor, and returned to the process via a dust collector hood. The cement on the turntable is leveled for presentation to the X-ray beam via a two stage leveling system.

Once leveled the sample turns continuously past the X-ray beam, and the resulting diffracted X-rays are detected over a complete range of angles, generating a complete diffraction pattern. A scraper is mounted in the sample presentation stage to remove the cement after it has turned past the X-ray beam. The scraper clears the turntable prior to the continuous sample feed point ready to receive more cement, and the removed cement is returned to the process via the venturi vacuum system.

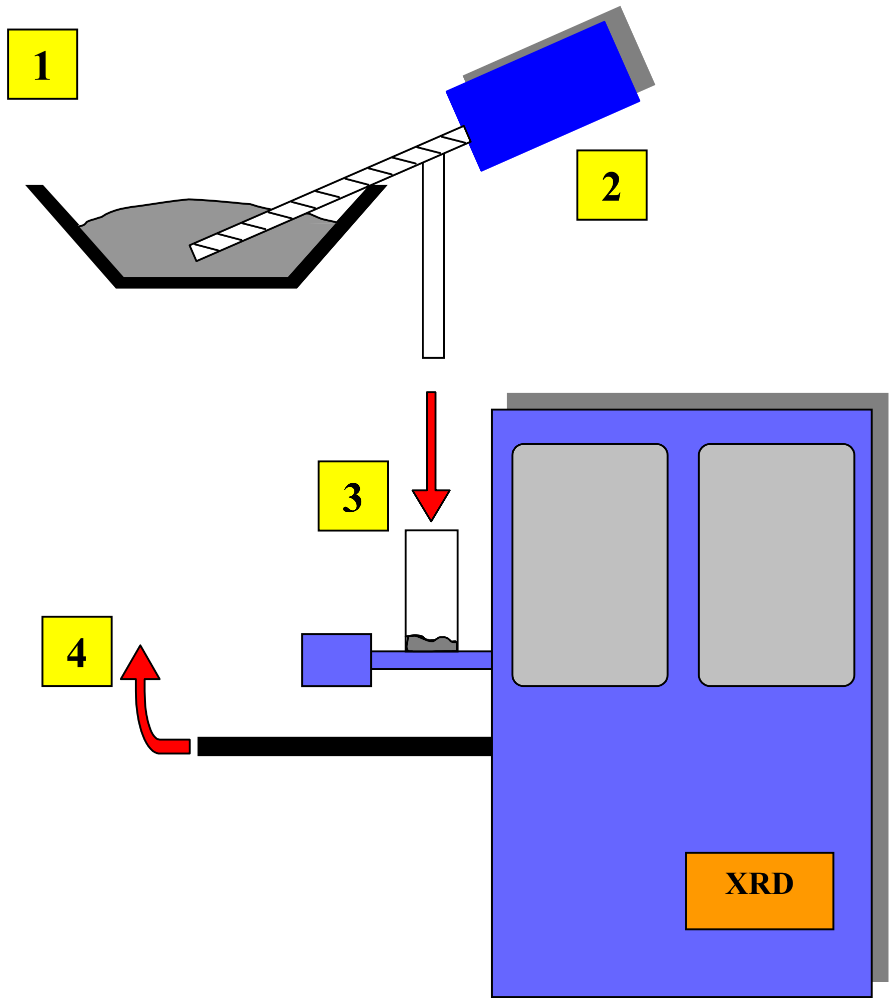


Figure 3. Schematic of sample extraction and return

As stated above the cement sample is presented to the X-ray beam as a flat moving bed. The X-rays are produced by an X-ray tube, and collimated by emerging from the X-ray beam tube slits just before the sample. When the X-rays interact with the sample bed they diffract from the thousands of crystals in a pattern that is characteristic of each particular crystal. The diffracted X-rays are detected by a special detector that is able to collect X-rays over a wide range of angles, in this case 120 degrees. This detector collects the full range of the diffraction pattern simultaneously. The resulting diffraction pattern shows the peaks that are characteristic of the different types of crystals, dominated by the major phases, such as C_3S and C_2S. A typical diffraction pattern is shown in Figure 4, including some indicators of the origins of some of the peaks.

The data collection process is happening continuously, but the patterns are analyzed every minute, and are used to make up a rolling average pattern of ten minutes of data. The rolling average pattern is analyzed every minute by the analysis software, which uses a method known as the Rietveld analysis technique to determine the percentage of each mineral phase. Professor Rietveld first described the Rietveld technique in the late 1960's, but it is only recently that computers have become powerful enough

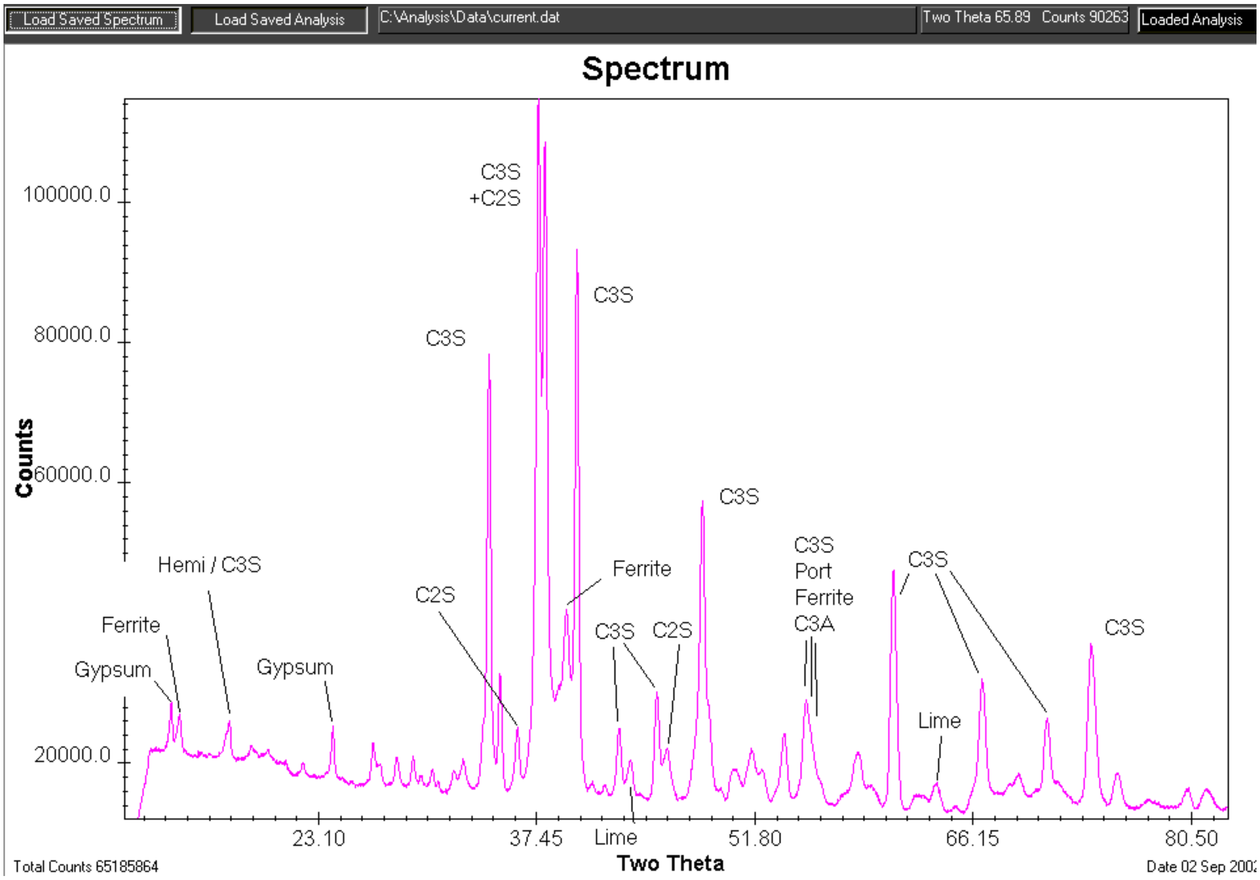
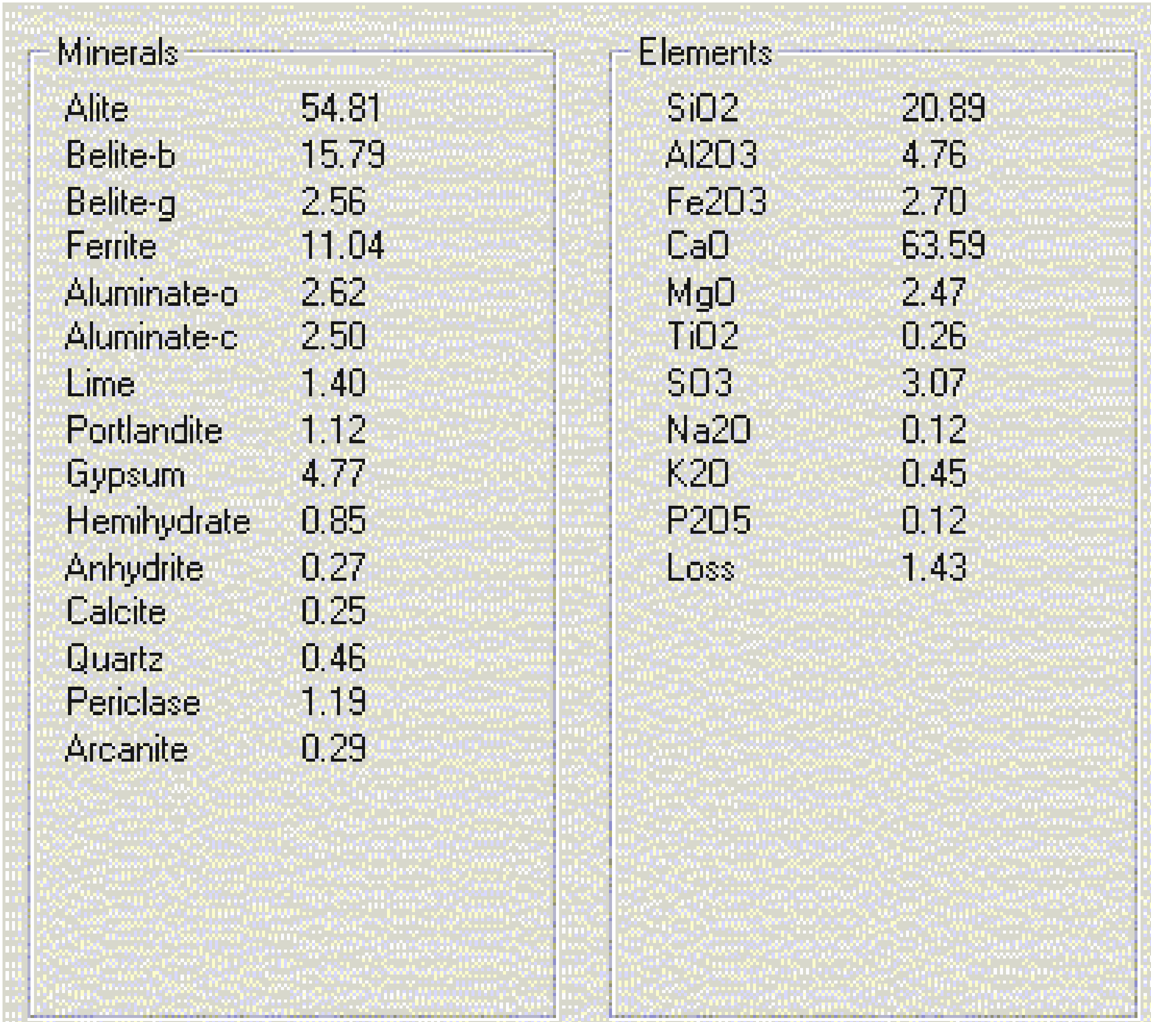


Figure 4. Diffraction pattern, measured by the full area detector.

to allow rapid routine pattern analysis. Basically the Rietveld technique reconstructs the measured diffraction pattern based on the fundamental physics of the microscopic interaction of the X-ray beam with the sample bed. This calculation uses the supposed composition of the cement sample as a starting point, and reaches a solution through a process of least squares optimization. The outcome of this analysis is a standardless quantitative analysis of the cement composition in terms of the individual mineral phases that are present. Note that the Rietveld analysis does not identify species from individual peaks, but rather uses the entire set of peaks that are characteristic of each species.

Figure 5 shows a list of the phases measured by this XRD analysis, and these include the full set of mineral phases that may be found in the cement, down to the detection limit of the technique. Included are the major and minor phases of alite, belite (beta, gamma), ferrite and aluminate (orthorombic, cubic). Other phases that are measured are the minor phases such as calcite, periclase (MgO), lime, portlandite, and arcanite (an alkali sulfate, K_2SO_4). The gypsum phases, including hemihydrate and anhydrite are also included in the analysis. Other phases may be analyzed if necessary, by configuration of the software input file.



Minerals	
Alite	54.81
Belite-b	15.79
Belite-g	2.56
Ferrite	11.04
Aluminate-o	2.62
Aluminate-c	2.50
Lime	1.40
Portlandite	1.12
Gypsum	4.77
Hemihydrate	0.85
Anhydrite	0.27
Calcite	0.25
Quartz	0.46
Periclase	1.19
Arcanite	0.29

Elements	
SiO2	20.89
Al2O3	4.76
Fe2O3	2.70
CaO	63.59
MgO	2.47
TiO2	0.26
SO3	3.07
Na2O	0.12
K2O	0.45
P2O5	0.12
Loss	1.43

Figure 5. Phases measured by the continuous XRD.

<u>Results in Service</u>

Shortly after the XRD was installed a comparison was made between the analysis results and the settings of the gypsum weighfeeder. This comparison showed that there was good agreement between the analyzer and the weighfeeder. Figure 6 shows the plant weighfeeder as the solid line and the XRD results as single dots for each minute's result. The times for the data were shifted to match the features in the trend, and this shift is accounted for by the transit of the gypsum on the mill feed conveyor, residence time in the mill, dust collector, cement cooler and the XRD sampling Auger and feedscrew.

As expected, the results of this comparison show the analysers raw gypsum percentage mirroring the weigh feeder totaliser results. This can be seen most clearly in the sudden dip in gypsum feed rate at around 3am on October 19, due to problems with the gypsum feeder, and then the step upwards at around 7am on October 19, due to a type change from Type V cement to Type I. The analyser raw gypsum was back-calculated according to all of the mineral components in the gypsum. In other words the raw gypsum percentage is calculated from the gypsum, hemihydrate, anhydrite and minor amounts of calcite.

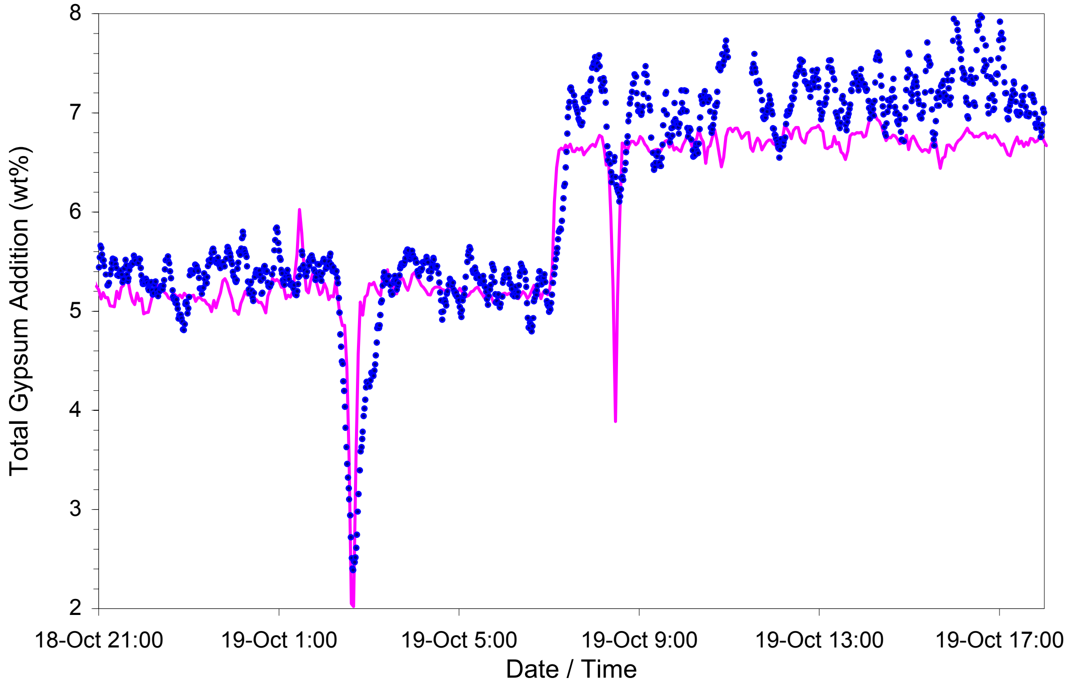


Figure 6. Trend of XRD calculated gypsum vs weighfeeder

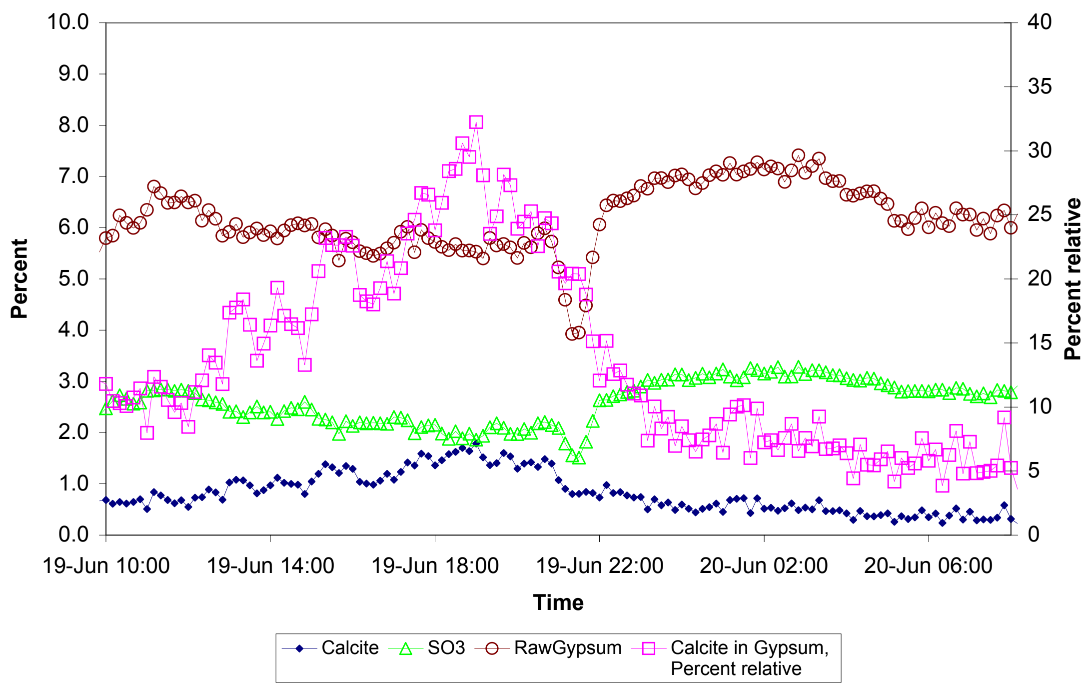


Figure 7. Time of poor gypsum quality.

Figure 7 shows the trend for a time that the gypsum quality was questionable. On a number of occasions the XRD results have revealed problems with the gypsum supply. The gypsum is supplied from a local quarry and loaded into the gypsum silo by truck. The gypsum feed normally contained some calcite, typically about 5%. On this particular occasion the calcite in gypsum increased to about 30%. This was thought to be due to the supplier reaching the end of a stockpile and scraping the ground under the stockpile, which happened to be high in limestone. The consequence of high levels of limestone in the raw gypsum feed was that the percent of SO3 in the finished cement dropped to well below the set point. At the time the plant was making Type I-II cement with a set point of 2.7% SO3. As the percentage of calcite in the gypsum increased the percent of SO3 in the finished cement decreased, even though the feed rate from the gypsum weighfeeder was set at the normal level. Consequently the gypsum feeder settings had to be raised by 5% to achieve the 2.7% SO3 set point, and the resultant cement had 5% less clinker in it.

The problem as described above was identified in hindsight, through following the trends from the XRD analyzer. These trends clearly showed the increase in calcite, and the supplier was thus identified as causing this particular incident. With the XRD information the outcome was that the supplier could be instructed clearly about the requirements for the gypsum supply – ie. constant quality to avoid SO3 excursions.

A further outcome of this type of incident is to build the confidence of the operators. By taking grab samples and finding a valid cross check against the XRD the operators are able to recognize the value of the analyzer data, and understand the interpretation of the trend data.

Trends of major cement phases

The trends in Figure 8 to Figure 10 are some examples of the mineralogical data that is available from the XRD. Note that these are the actual mineral phases that have been measured, and this is not always represented by the traditional Bogue calculation based on the oxide measurements. The difference between the quantitative measurement of the mineralogy and the Bogue calculation is most apparent in the comparison between the Aluminate and Ferrite phases. In these cases the Bogue calculation over estimates the percentage of Aluminate present and under estimates the percentage of Ferrite, however the trends can still be clearly seen.

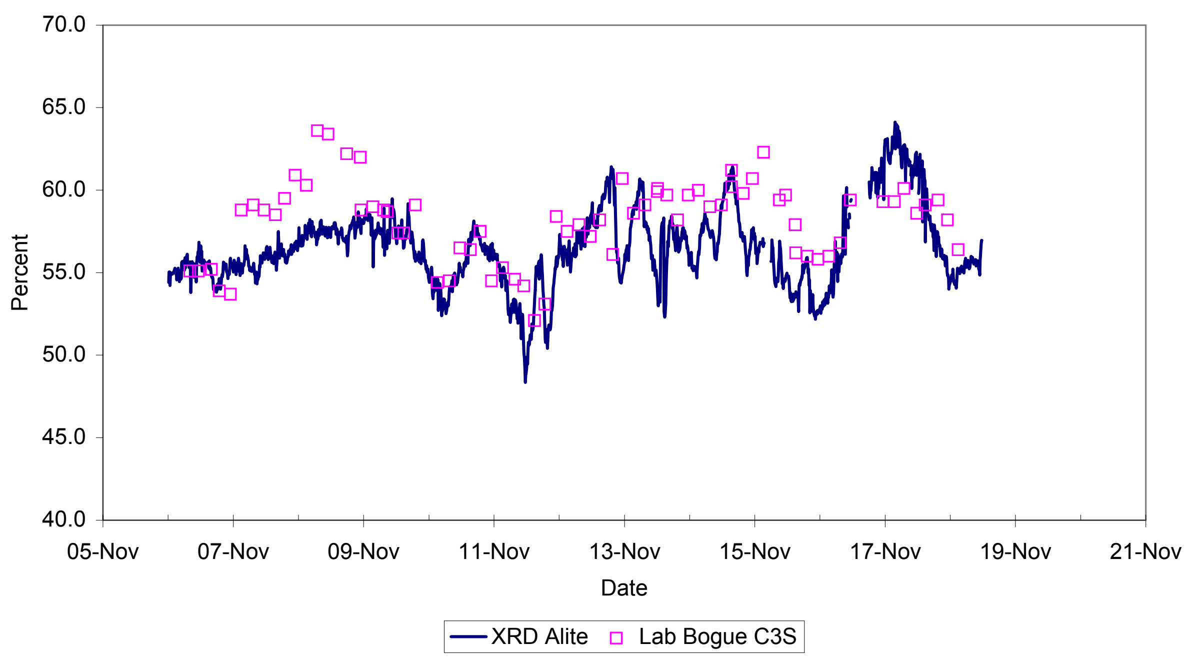


Figure 8. Trend of XRD Alite compared to Bogue C3S calculated from laboratory XRF oxides.

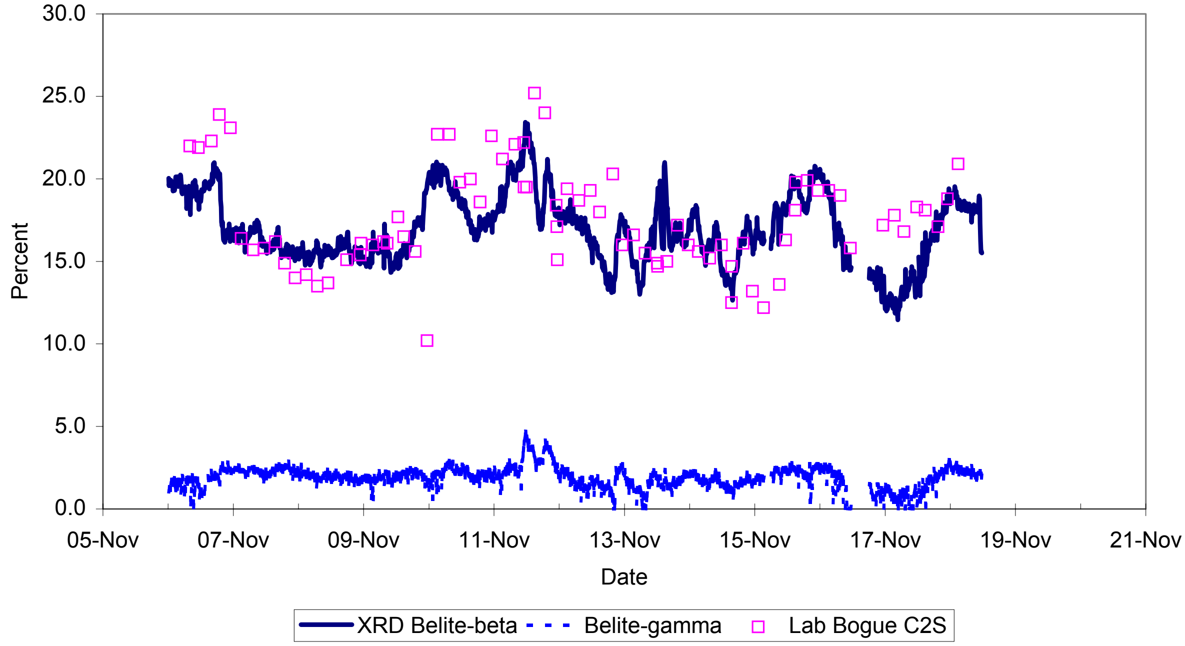


Figure 9. Trend of XRD Belites compared to Bogue C2S calculated from laboratory XRF oxides.

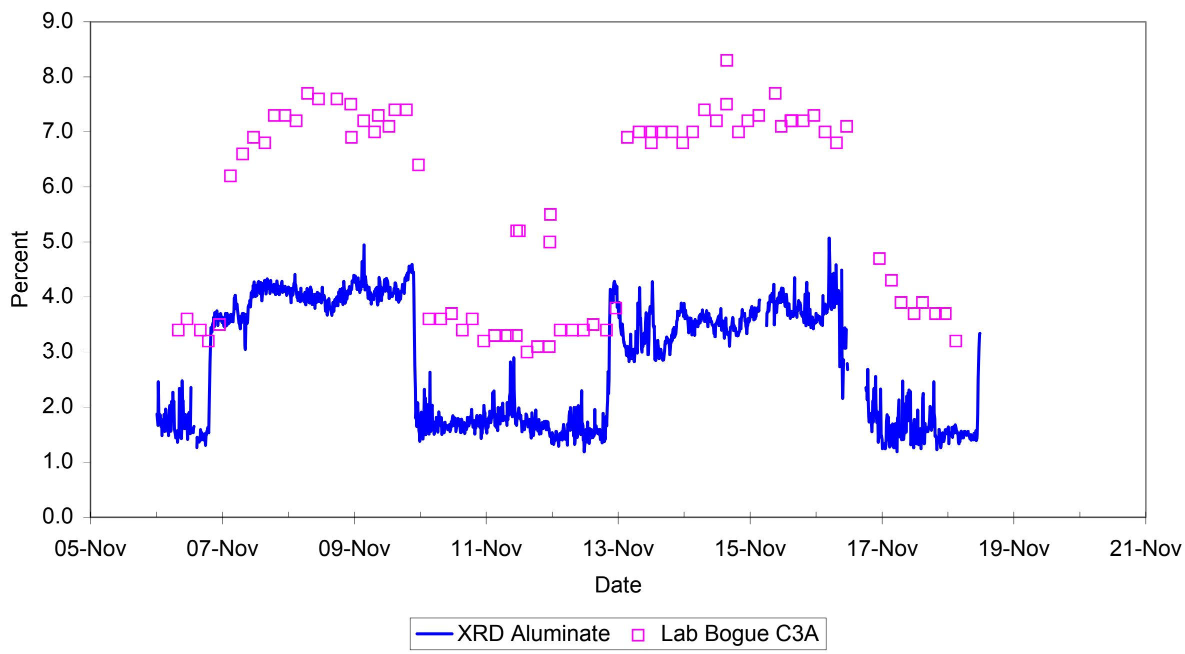


Figure 10. Trend of XRD Aluminate compared to Bogue C3A calculated from laboratory XRF oxides.

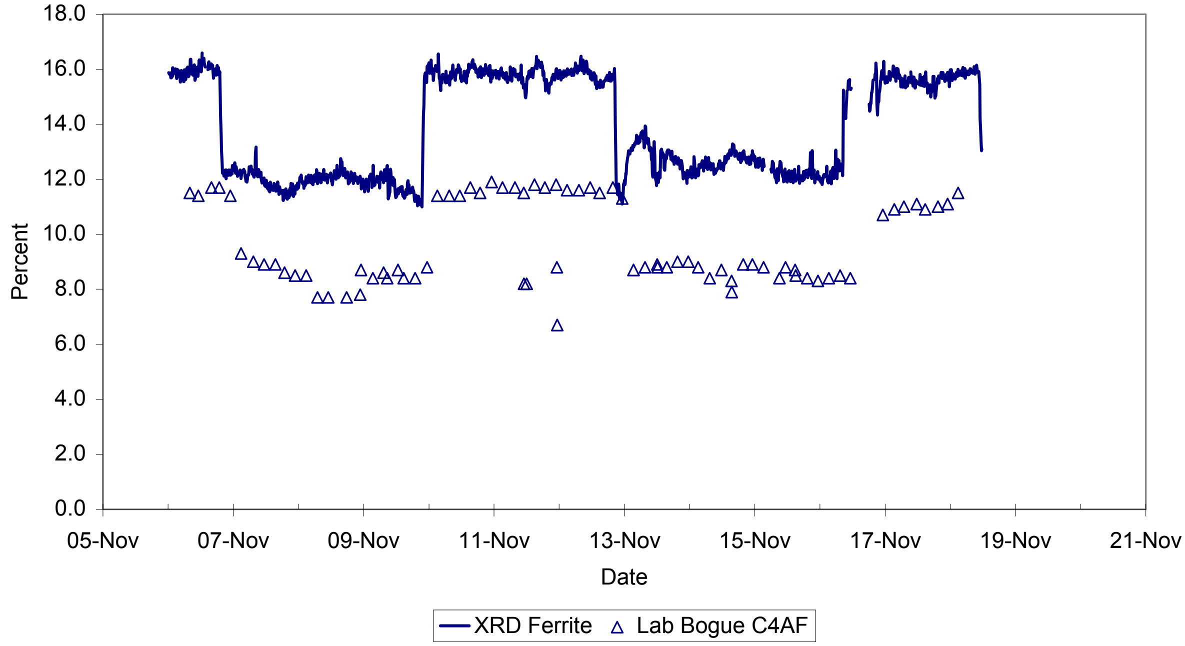


Figure 11. Trend of XRD Ferrite compared to Bogue C4AF calculated from laboratory XRF oxides.

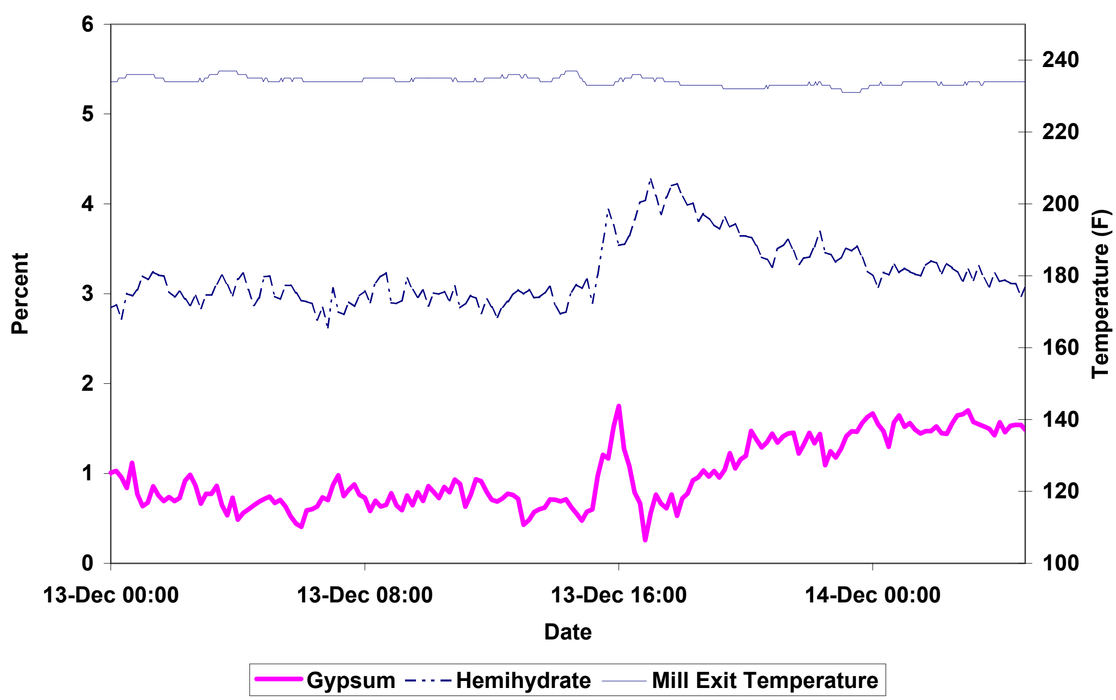


Figure 12. Trend of gypsum and hemihydrate

In the trends of gypsum and hemihydrate shown in Figure 12 the variations in the relative quantity of these phases can be clearly seen. While it has not yet been possible to identify direct cause and effect there is clearly a case for maintaining a fixed ratio for consistent cement behavior. Traditionally controlling the mill exit temperature is used to maintain constant gypsum dehydration, but monitoring of gypsum states continuously has shown that this dehydration can vary dramatically even with constant mill exit temperature.
The ratio of hemihydrate to gypsum may change dramatically if the temperature of the clinker entering the mill changes for example. The amount of hemihydrate present is known to be a factor in false and flash setting of cement, and also controls setting times and influences early strength development.

Free Lime Analysis

In the trends shown in Figure 13 and Figure 14 the free lime in the cement can be seen to vary significantly throughout the day. The rate of change in these variations is completely masked by the traditional composite sample result that most plants use for quality control, shown by the solid lines. Variation like this is not normal, however through the judicious use of on-stream control systems this type of variation can be identified and reduced. In this case for example, the control would be enacted at the raw mix or pyro-processing stage of production. In Figure 14 the C3S and C2S measured at the same time are also shown. The reduced C3S and enhanced C2S clearly shows that in this case the higher free lime measurement was due to underburning of the raw material.

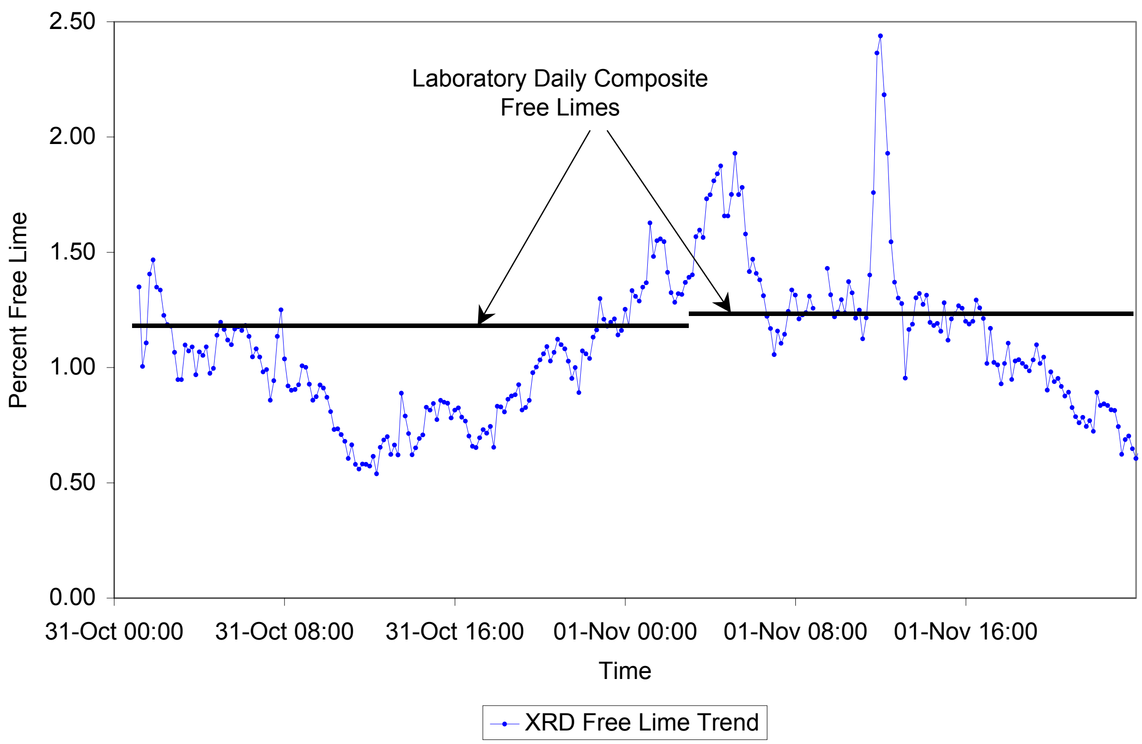


Figure 13. Trend of Free Lime.

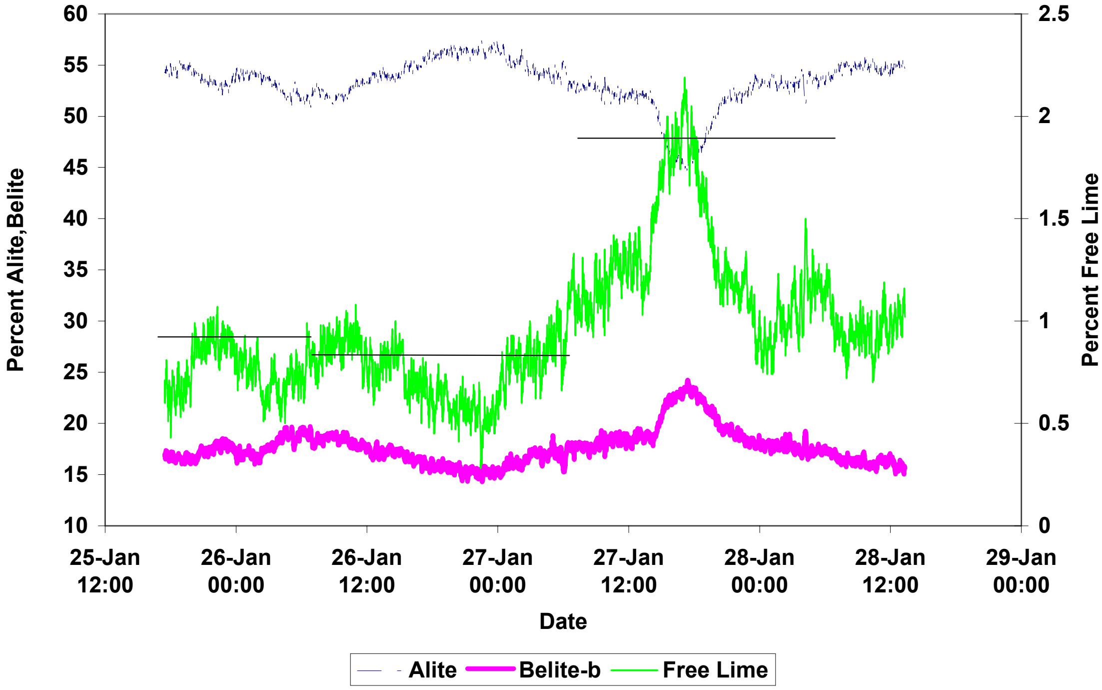


Figure 14. Free lime excursion, showing reduced C3S and enhanced C2S.

<u>Comparison with lab XRF oxide analyses</u>

A series of comparisons have been made with the traditional XRF analyses that are taken of the four hourly samples from the laboratory. In general these show very consistent results, as illustrated by Figure 15 and Figure 16. Note that the XRD derived oxides are calculations based on a fixed oxide composition of the different phases. The oxide compositions of the various phases have been determined in advance by detailed electron microscopic analysis of a range of individual crystallites.

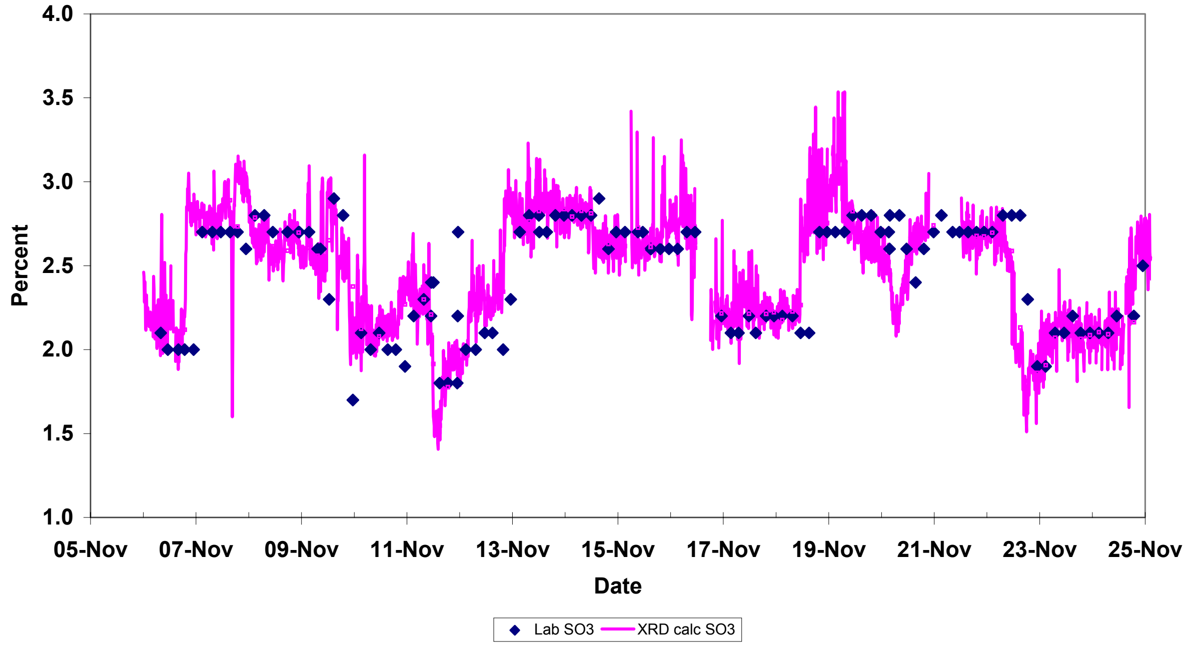


Figure 15. Comparison between Lab XRF SO3 and XRD calculated SO3

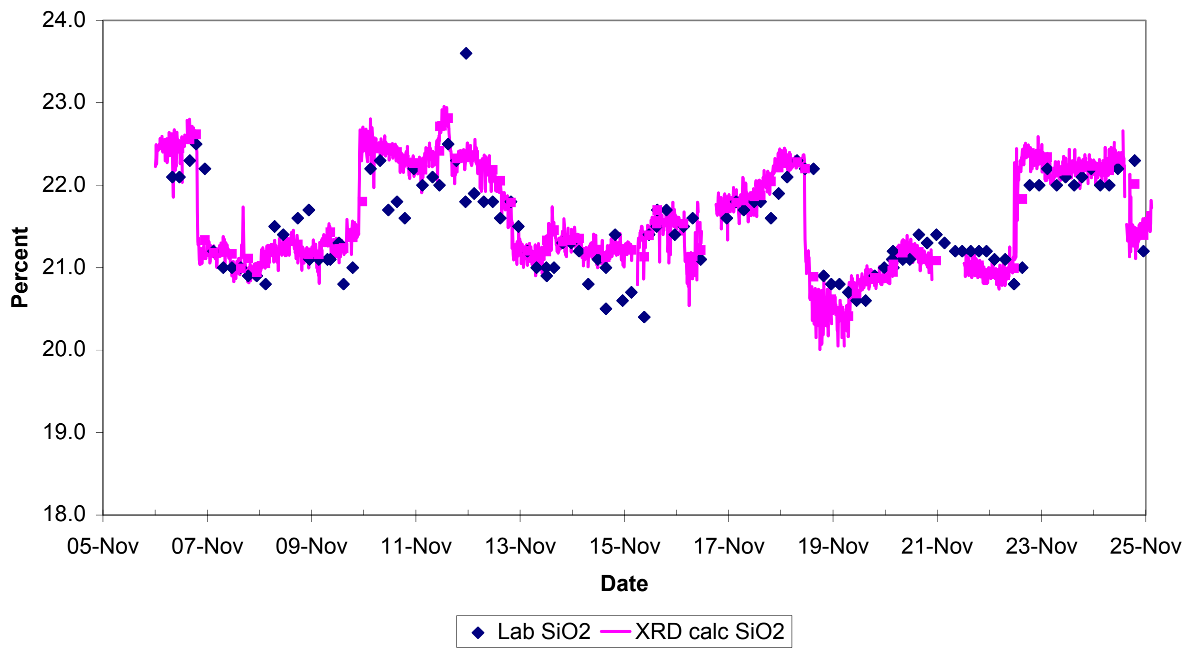


Figure 16. Comparison between Laboratory XRF SiO2 and XRD calculated SiO2.

Predictive Work

The XRD data has been used along with fineness data from an on-stream particle size analyzer to develop strength predictions for the cement as it is being produced. This system has a number of advantages over the traditional ASTM strength measurements. The standard ASTM test is performed on a composite sample that is developed over a period of about 24 hours. The test result is therefore an average result for that 24 hour period, and it may be difficult to detect any variations in the cement quality throughout the period. Further to this there is the standard delay in obtaining the physical test data since the results are not available immediately. In contrast the on-stream predictions are provided on-stream in real time. This enables the quality of the cement sent to the silos to be carefully monitored, and allows the possibility of corrective action before the cement is shipped out or even maximizing mill production by increasing mill feed if cement strength is over target.

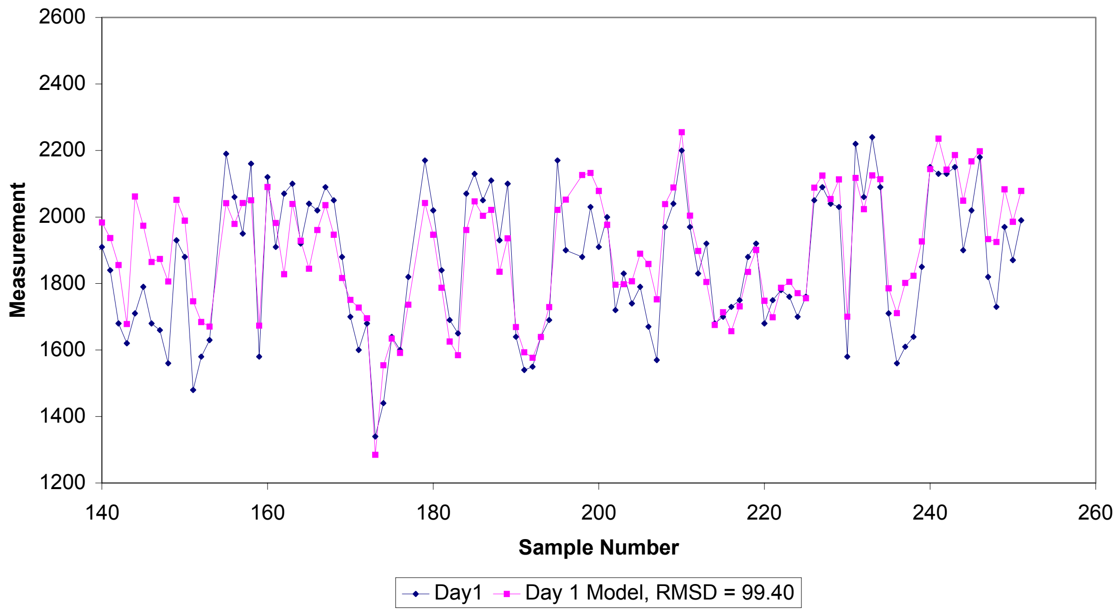


Figure 17. Strength predictions

At present the strength predictions are working reasonably well for the 1, 3 and 7 days periods, however the predictions for the 28 day period are not yet as good. We are working on improving the quality of the 28 day predictions. Consistency of cement produced is very important for the ready mix market and the on-stream XRD has a huge potential to help the plant to achieve consistency in the final cement product.

Conclusion

The continuous XRD has provided the plant personnel with an invaluable window into their process, and this real time information is used at all levels, from the control room operators through to the chief chemist and plant manager. Decisions regarding quality are now made in a timely manner, backed up by the continuous trends provided by on-stream analysis, rather than single sample analyses.

A significant future benefit of the on-stream XRD is to allow the possibility of reducing the operating and labor costs. Eventually, on-stream analyzers will be used for all of the routine analysis activities at the Leamington plant, and the continuous XRD analyzer is a vital part of this plan. In this case the introduction of on-stream analysis has allowed the control of the gypsum weigh-feeders to be transferred to automatic control. Work is continuing on the area of physical test prediction with the aim of providing on-stream and continuous measures of the cement strength and setting times.

Finally, it can now be said that the technologies exist for continuous on-stream monitoring and control of a cement plant from a quality perspective. This makes the need to take periodic samples from the process streams back to the control laboratory for testing redundant. The benefits for a fully automated quality control system will be large, leading to optimized operation for kilns and mills, more consistent product quality and reduced labor requirements.