Continuous On-line Measurement of Cement and Clinker Mineralogy for Quality Control and Optimisation Using X-ray Diffraction

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Abstract

Continuous on-line measurement of cement mineralogy is now becoming accepted into the cement industry. Following the first commercial installation in late 2001, continuous on-stream X-ray diffraction analysers are now operating in four different countries around the globe. A sample extracted from a production stream is passed continuously through this type of X-ray diffraction analyser. The collected data is automatically processed via preconfigured Rietveld refinement to determine the percentage of each different mineral present in the sample. Analysis of a continuously moving sample stream offers a number of technical advantages and provides the cement producer with a detailed trend of mineralogical composition. By multiplexing the sample delivery a number of different sources can be analysed. Data showing significant real time variations in production cement mineralogy including free lime, portlandite and gypsum hydration states will be presented and discussed. Using this information to optimise the production process is also discussed.

1. Introduction

In recent years X-ray diffraction (XRD) has become a common means of directly measuring cement and clinker mineralogy. In cement production, laboratory XRD will typically involve the analysis of a small amount of material which has been sampled from the production process. In the case of a sample that has been taken over a two hour period, that sample could represent production in excess of 200 tonnes of cement or clinker and yet still only provide a single average analysis result based on a few grams of material. In a Continuous On-Stream Mineral Analysis (COSMA) system the sample is passed through the analyzer at the rate of about 100 grams per minute, so the sample can much more easily represent the bulk production stream. Results in this system are reported every minute, so that the trends in mineralogy can be clearly seen and related back to changes in the process.

The first commercial installation of COSMA was in October 2001 at the Leamington plant of the Ash Grove cement company in Utah, USA [1]. Since then COSMA has also been installed in Canada, Australia and Italy and further installations will be made in Italy and the USA in the near future.

COSMA is possible through a combination of a unique sample presentation stage, a position sensitive X-ray detector and Rietveld analysis, providing mineralogy of cement and clinker from a continuous stream of sample. The material fed to the analyser is extracted from the production process via a sampler and presented to an internal turntable by a feed screw. Sample on the turntable is presented for X-ray diffraction analysis after preparing a precisely located flat bed of material, which moves continuously under the X-ray beam, allowing data to be acquired from a large number of sample crystallites. Data acquisition is by a large, stationary, position sensitive X-ray detector, which continuously collects up to 120 degrees of diffracted X-rays from the sample. Results are presented after analysis by preconfigured Rietveld analysis software.

2. Sample Presentation

Powder X-ray diffraction analysis has specific sample presentation requirements. It is necessary to ensure that the detected X-rays are proportionally representative of each of the possible reflections from each of the mineral phases present in the sample. This is typically achieved by fine grinding of the sample and sample spinning. Some of the fineness requirements for XRD have been discussed in general by Smith and specifically for cement by Enders [2,3]. In continuous XRD the sample is moved continuously past the X-ray beam.

With a moving sample bed streaming past the X-ray beam, each point on the sample bed spends no more than about 1 second in the X-ray beam, when the turntable is rotating at about 1 rpm. In this way a very large number of crystallites and orientations are examined during a given analysis period. By moving the sample continuously through the X-ray beam the sample preparation requirement is significantly reduced – no further grinding is required for cement and clinker can be presented after grinding to only 50% passing 45microns. The significance of moving the sample can be seen in Figures 1 and 2, where patterns have been acquired with the sample turntable stopped in several positions compared to a series of patterns acquired for the same period of time with the turntable moving. In both figures the data has been accumulated for 180 seconds by the 120 degree position sensitive detector, using cobalt Ka radiation from a tube running at 35kV and 35mA. Clearly the patterns with the turntable moving are much more representative of the bulk sample.

Note that having an large number of particles examined in each analysis period is a significant factor in obtaining a representative pattern for analysis. Another factor that must be considered is microabsorption. Microabsorption has been discussed in detail in the literature, and can be a strong effect for larger particle sizes [4]. Since cement and clinker phases appear in a matrix many particles will have more than one phase and the orientation of individual particles can significant, since lower phases can be masked by upper phases. Furthermore, interstitial phases can be found inside larger particles and these can be masked by the enveloping phases. For cement and clinker strong microabsorption effects can be seen for iron when copper Ka radiation is used since the iron absorption edge starts just below the copper Ka energy. The effect of iron absorption and fluorescence has been minimized in this case by using cobalt Ka, which has a lower energy that is unable to cause iron fluorescence.

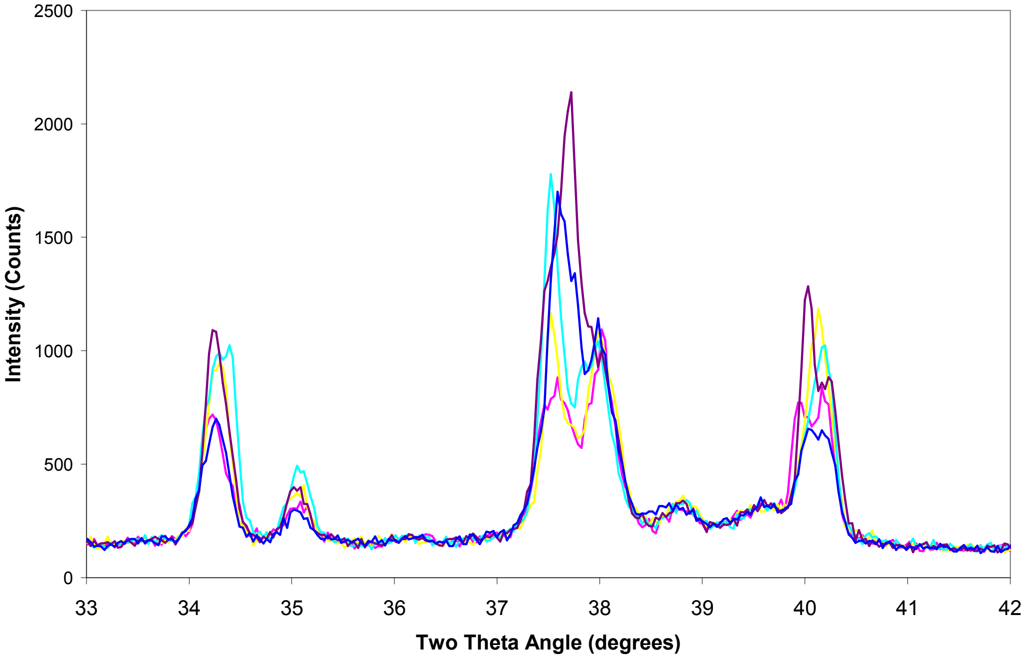

Figure 1: Patterns collected from several positions using a stationary sample of cement.

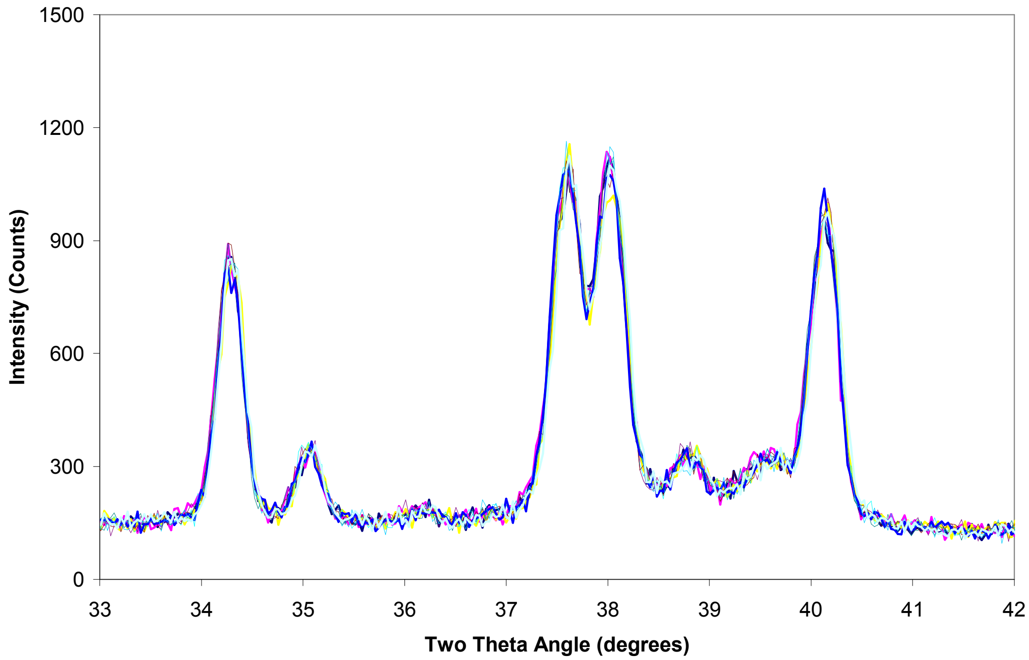

Figure 2: Patterns collected from the sample of cement while on a rotating turntable.

3. Sample Preparation Effects

A particular advantage of the minimal sample preparation requirement can be seen in the analysis of cement which contains gypsum ($CaSO_4.2H_2O$), which in the finish mill may be converted to bassanite or hemihydrate ($CaSO_4.½ H_2O$) due to elevated temperatures. From a cement producers' and users' perspective the hydration state of $CaSO_4$ is relevant due to the effects on the macroscopic properties of the concrete or mortar in which the cement is used. Mortar setting time can be significantly affected by the percent of hemihydrate present compared to the percent of gypsum, due to the much higher solubility of hemihydrate compared to gypsum [5]. Too much hemihydrate can lead to false set, while insufficient hemihydrate can lead to flash set. XRD analysis of $CaSO_4$ hydration in cement can be difficult in the laboratory, since the cement should be ground finely for accurate analysis. Fullman and Walenta have shown that from excess grinding the gypsum may be converted to hemihydrate or to an amorphous phase [6]. With the minimal preparation requirements of COSMA these changes are avoided since the sample is measured as received, direct from the production process, leading to good accuracy in measuring gypsum and hemihydrate. An example of the accuracy for hemihydrate can be seen in Figure 3 where known amounts of hemihydrate were mixed with clinker and analysed, with an accuracy of better than 0.19% root mean squared deviation without bias correction and 0.11% standard deviation.

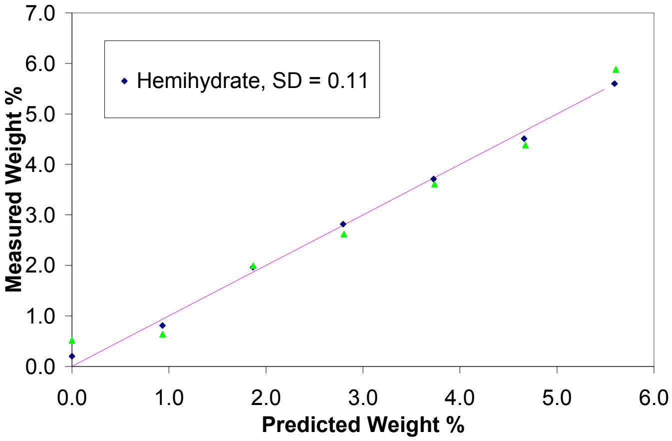

Figure 3: Accuracy of hemihydrate measurement using XRD

Accurate data analysis is achieved using fundamental parameters Rietveld analysis. The fundamental parameters technique uses the physical properties of the analyser to determine factors such as the variation of peak width with angle. This analysis technique minimizes correlations between parameters and maximizes the stability of the complicated non-linear mathematical solution. The fundamental parameters approach to Rietveld analysis has been reviewed in some detail by Cheary et al [7]. Using Rietveld analysis provides the complete mineralogy of the sample, based on a 100% normalization of the mineral phases included in the analysis.

4. Trended Results

Using COSMA, cement and clinker producers are able to rapidly build up a large database that represents their production mineralogy. This database allows trends to be generated which clearly show the reaction of the product to changes in raw materials, pyro-processing changes including fuel changes and changes in grinding conditions. In turn this information can allow the producer to optimize the process and quality through correct and timely reactions to variations and events in the process.

For example, continuous mineralogical analysis trend charts shown in Figures 4 and 5 show the effect of a single finish mill stoppage, after the mill was crash stopped due to a drive failure. The mill was full of product when it stopped and the trend shows the composition of the cement after the mill was restarted. The product has been affected by the residual heat and resulting moisture in the mill. At the temperatures in the mill the main thermal changes that can occur are in the hydration of the gypsum. In this case the gypsum percentage has decreased, with a corresponding increase in hemihydrate. In addition there is a clear change in the portlandite ($Ca(OH)_2$), which has increased in response to the excess water released from the gypsum. Portlandite is hydrated free lime but the decrease in the product free lime is not sufficient to account for the observed increase in portlandite. However, based on the observed decrease in the alite we can conclude that the extra portlandite is a result of the reaction of the alite to the excess water that has not been swept from the mill after the crash stop.

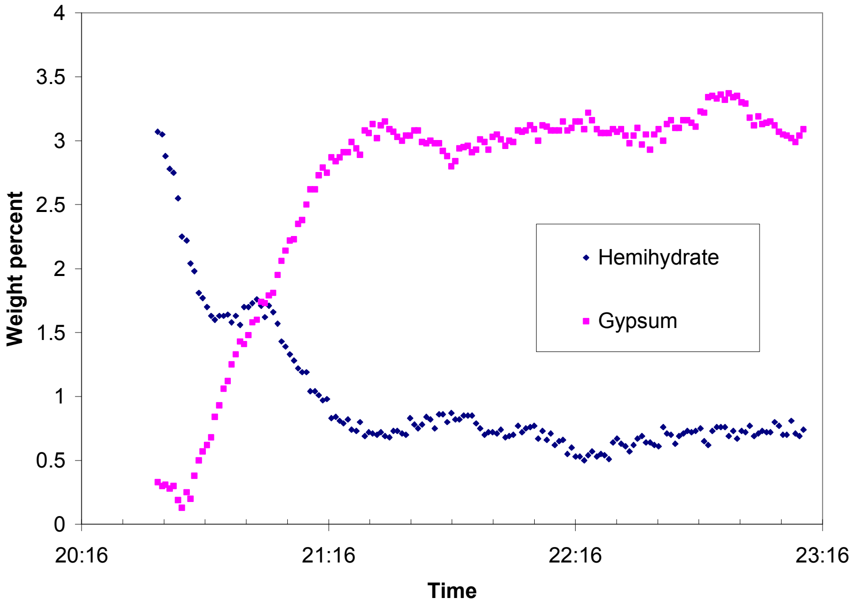

Figure 4: Changes in Gypsum Hydration As a Consequence of Mill Stoppage

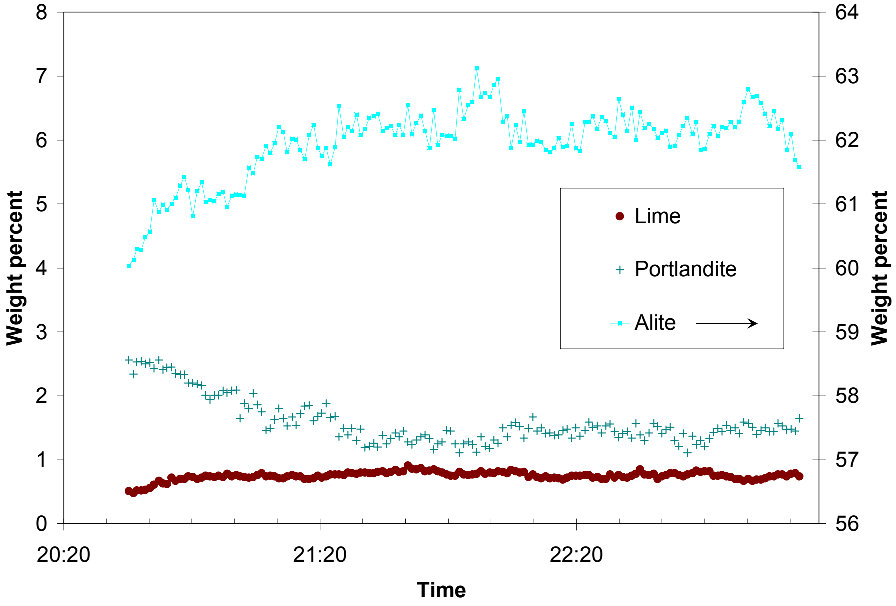

Figure 5: Changes in Gypsum Hydration As a Consequence of Mill Stoppage

Normally $CaSO_4$ hydration in the finish mill product is controlled by the application of cooling water sprays at the exit of the finish mill and also sometimes in the centre compartment. These sprays are typically adjusted according to the temperature of the finished product, with the intention of maintaining constant hydration. The hydration reactions are quite sensitive to temperature, so the theory is that by controlling the mill exit temperature to a constant value the product hydration is controlled. In practice however the product hydration is affected in a more complex way by the influence of other factors such as the temperature of the clinker as it enters the mill and to a lesser extent by the temperature of the air that is sweeping the mill system. Figure 6 shows time based trends of a mill system in which we can see that the hemihydrate fraction has varied significantly while the exit temperature has been maintained constant. In this case the variation was due to the increased temperature of the clinker entering the mill that can be seen in Figure 7, which coincides with the change in gypsum to hemihydrate ratio.

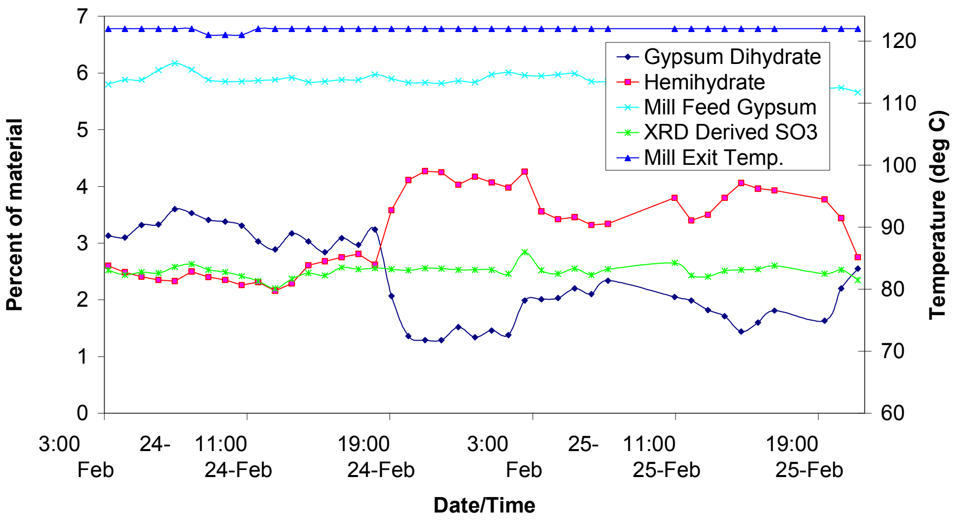

Figure 6: Changes in gypsum to hemihydrate ratio in the finish mill

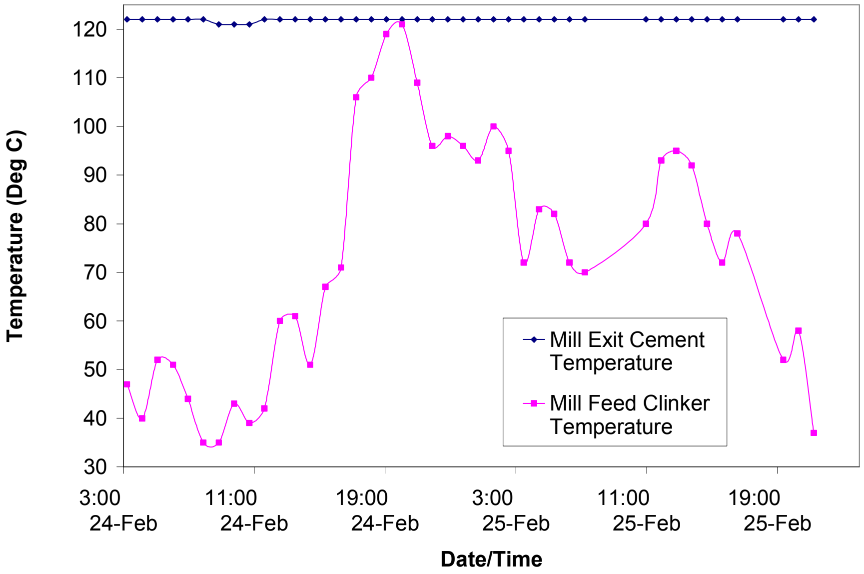

Figure 7: Change in the clinker temperature entering the mill

5. Limestone Addition and Control

Using COSMA the addition of limestone at the mill can be accurately and continuously controlled. This ensures that the product is compliant with standards while allowing the maximum addition. By using the maximum addition the production of cement can be maximized at the minimum cost since the cost of using limestone is less than the cost of clinker. In many cases a conservative approach is taken to ensure that the product always meets specification, however with continuous analysis and control the product composition can be controlled more accurately.

Under North American standards, the usual limiting factor in limestone addition is the restriction on loss, or split loss, (split loss refers to the test designed to isolate CO_2 loss from water loss), by considering the difference between the loss at 550 and 950 degrees. Using COSMA results it is possible to calculate the expected loss, based on the different mineral phases present in the cement. Knowing the reaction of the individual mineral phases to changes in temperature it is also possible to calculate the split loss and use this for real time control of the limestone addition.

Typical control of the limestone addition is via weighfeeders, which can work quite well when the weighfeeders are accurate, however it is an indirect method. If for example the limestone quality varies, or some gypsum is inadvertently added to the limestone silo, then the rate of addition will not be as expected from a simple weighfeeder setting. Using

COSMA it is possible to control the addition from a direct measurement. An example of this direct measurement is shown in Figure 8.

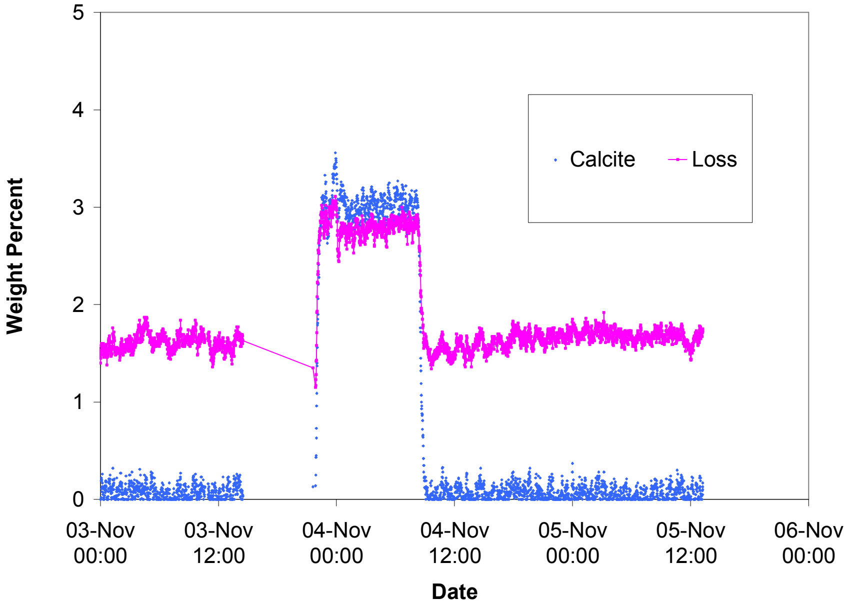

Figure 8: Trend showing a cement type change with limestone addition

6. Clinker Control

There are a number of areas where COSMA in clinker production can be used to improve the production process. It is generally understood that an optimal burn of kiln feed to clinker is can be achieved by reacting the clinker until the free lime is reduced to about 1.2 to 1.5%. In practice it is easier for a kiln to be operated under harder burning conditions, with concurrently lower free lime, so in many instances kilns are producing over burnt clinker. Over burnt clinker tends to be less reactive, harder to grind and uses more fuel than clinker burnt to optimal free lime. Under burnt clinker is easier to grind, but comes with the risk of making unsound (expansive) mortar, particularly if the free lime exceeds around 3%.

With COSMA the free lime can be reported to the kiln control system on a much more frequent basis, leading to better control. In addition the trending of information on the clinker mineralogy will offer greatly enhanced diagnostics. For example the free lime in a clinker may increase due to over-limed raw mix or due to the clinker being under burned. These two situations can be immediately distinguished using COSMA, since in the case of under burning the clinker will show a clear tendency to have reduced alite and increased belite in association with the increased free lime (Figure 9). On the other hand a high free lime due to over-limed raw mix will appear in association with higher alite, as shown in Figure 10.

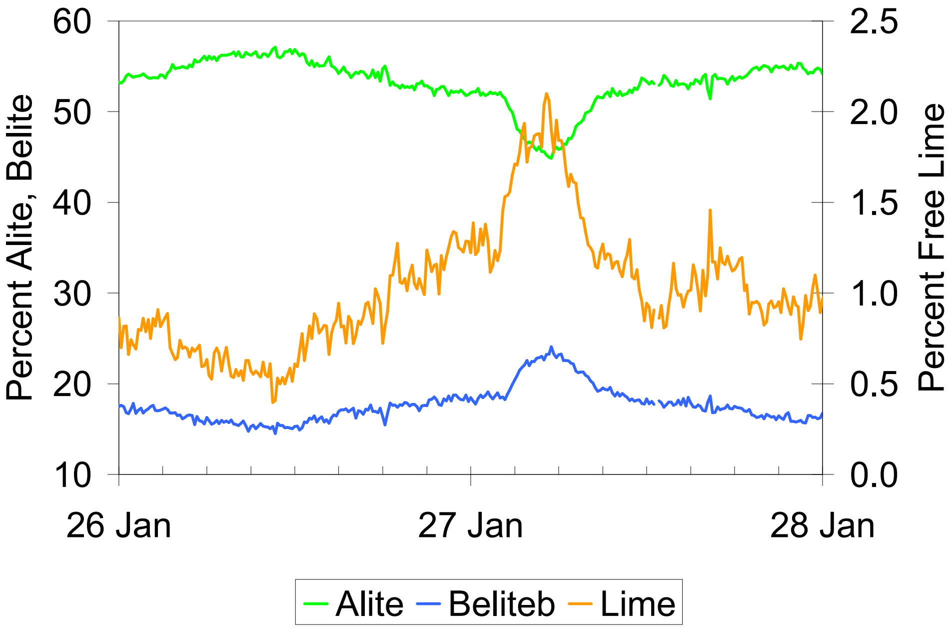

Figure 9: Free lime excursion due to underburning

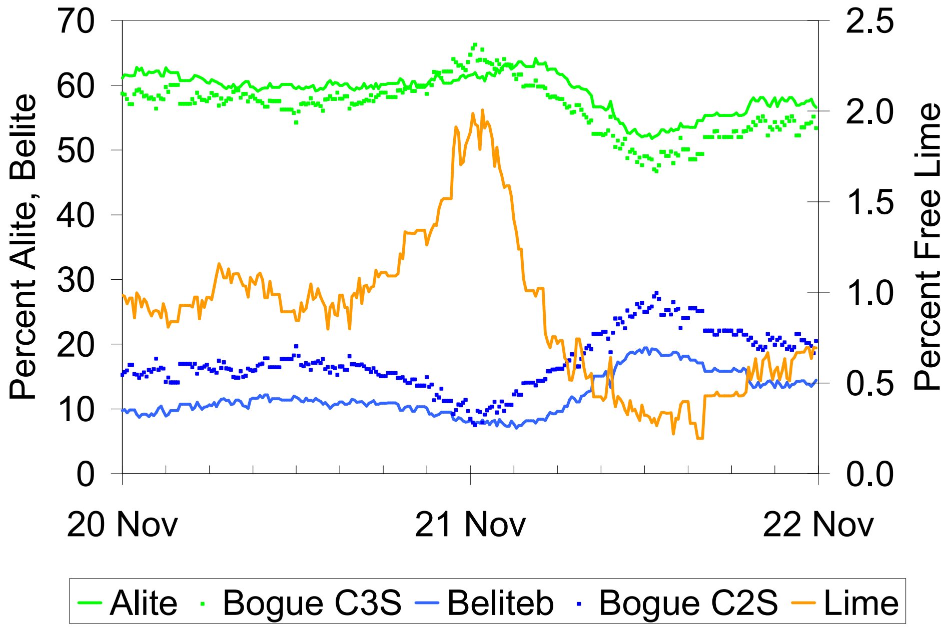

Figure 10: Free lime excursion due to excess Ca in kiln feed

One of the compelling factors for introducing COSMA is to offer intelligent control systems information that can be used to further optimize the kiln control. The full advantages of using COSMA for clinker production have not yet been realized. At this stage there are no installations on clinker. Many factors are used to control the kiln, including burning zone temperature, back end gas analysis, exit gas analysis, but all of these measures are used as indirect predictors of the product quality. At the end of the day it is the clinker mineralogy that matters, and by monitoring the mineralogy on a continuous basis it is possible to determine stronger correlations between the kiln behaviour and mineralogy. This in turns offers the opportunity to optimize the kiln behaviour.

It is possible to obtain data on several cement mills or kiln systems using a single COSMA, provided a suitable sample can be delivered from the individual systems. Typically 100 grams per minute is used. Multiplexing of COSMA has been set up with a fast evacuation system for the COSMA feed hopper. Sample can be taken from each individual source and analysed on demand, which offers the potential for continuous trending along with the convenience of automated analysis of several different product streams.

7. Conclusion

The use of X-ray diffraction analysis in the cement industry is growing, thanks largely to the improved stability of modern Reitveld analysis software, which allows the user to obtain an accurate analysis relatively easily. COSMA allows the cement producer to see real time trends showing the mineralogical composition of their product. This information allows the producer to identify the effect of different events in some detail and thus provides the opportunity to optimize their production process. These optimizations could be as simple as directing out of specification product to fringe bins for later re-blending, or to use the mineral phase information as input to automated control systems to target levels of gypsum and limestone addition, hemihydrate fraction or even predicted properties of the product. In the case of clinker production COSMA offers the opportunity to closely control the kiln operation so that the optimum free lime clinker is produced, while providing a complete mineralogical picture that validates each control action.

References

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