Continuous On-Stream Mineral Analysis for Clinker and Cement Quality and Process Control.

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Introduction

Quality control in cement production is becoming increasingly important as the customer expectation for high quality cement increases. High quality follows from good process control, which in turn brings increased production. Over the last decade the use of continuous cross belt analysis for automatic regulation of raw materials has become prevalent in clinker production. Pyroprocessing turns these raw materials into the essential hydraulic minerals, such as alite (C_3S) and belite (C_2S) (Figure 1). For many years cement producers have relied on indirect methods for controlling and verifying these mineralogical results of the production process. Using X-ray diffraction it is possible to directly monitor the minerals responsible for cement strength. One way of controlling quality and ensuring optimum production is to monitor the essential minerals in real time using FCT ACTech's COSMA.

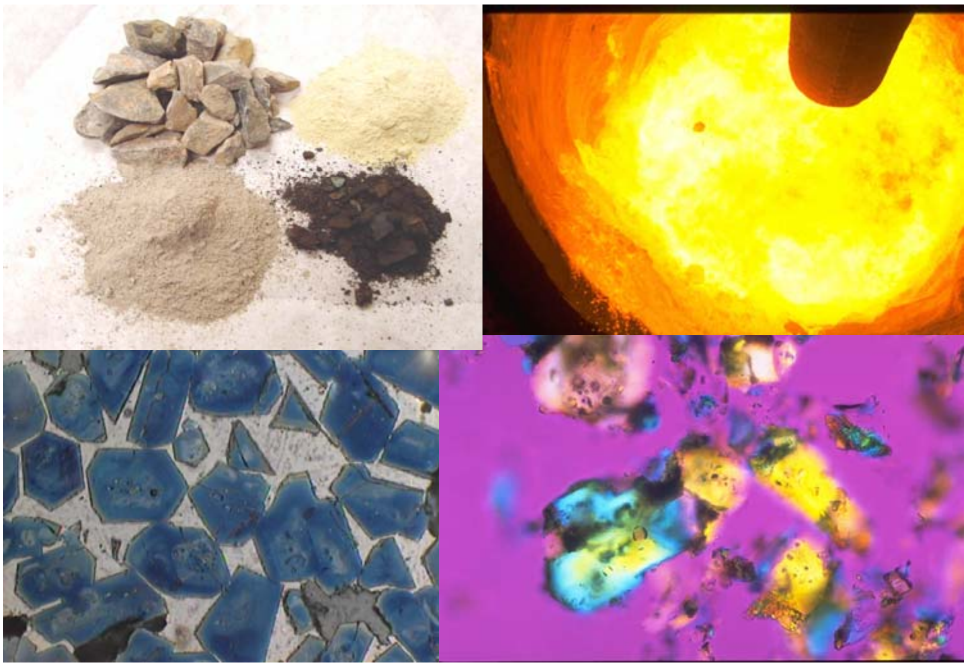

Figure 1: Limestone and other raw materials are pyroprocessed to clinker minerals.

Real Time Analysis

Process and product changes can at times be rapid. This is quite clear when observing the production of different cement types or monitoring the dehydration of gypsum in the grinding process. An example is shown in Figure 2 where limestone addition is monitored by the real-time COSMA analysis of the LOI and calcite percent during a product change from Type 1 to Type 10 cement and back to Type 1. With real-time analysis the operators and or the control system have no questions about the product so they can take action if required. If things go wrong, (equipment breakdowns or procedural changes) then the problem can be dealt with early, rather than waiting for an incorrect or out of specification product to be loaded or more seriously, shipped, or a silo to be filled with off specification material.

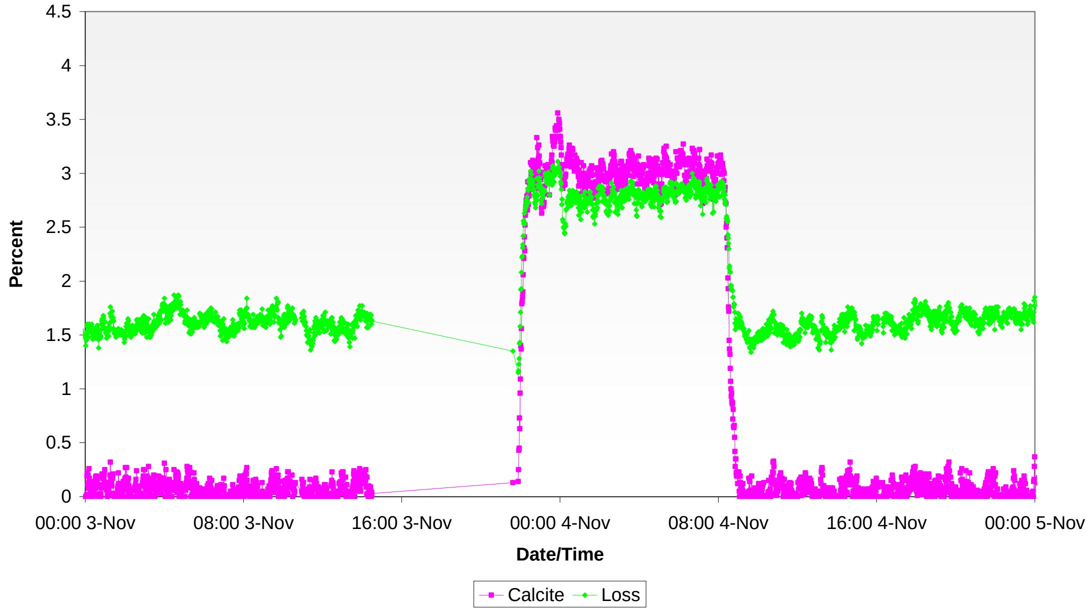

Figure 2: Transition between cement product types, showing the calcite measured by COSMA and the calculated LOI (loss).

COSMA is a proven technology that has been in use for several years.(Refs 1 and Refs 2). In terms of payback, one financial justification of a COSMA installation could well occur just by averting a single incident of incorrect product shipment, or by stopping off specification product from being loaded into silos. Later discovery of incorrect or out of specification product in production or shipping silos, or more seriously, having been shipped, can lead to expensive recovery or compensation costs. However, the real benefits of on line analysis are in the area of continuous process control, with automated dosing and regulation, and real-time feedback for operator and automatic control action.

Continuous Sample Presentation

X-ray diffraction relies on the match between X-ray wavelength and the spacing and alignment of crystal planes in the material under study. Any peak in an X-ray pattern is only produced under strict conditions of alignment between the X-ray beam, the X-ray detector and the crystal that is diffracting. The appearance of a diffraction peak at a given angle could be thought of as being similar to the effect that is seen when driving past an orchard or vineyard, as the different rows flash by. It is only possible to see directly down a given set of rows in the orchard when the observer (or detector) is positioned correctly with respect to the rows.

X-ray diffraction analysis of cement and clinker is not trivial. This is in part due to the complicated set of diffracted beams that can emerge from all of the different minerals that are present. Also, phases present range from the major clinker phases such as alite, belite, aluminate (C_3A) and ferrite (C_4AF) through to the minor phases including lime, periclase and alkali sulfates. In cement there are the gypsum ($CaSO_4.2H_2O$), hemihydrate ($CaSO_4.½H_2O$) and anhydrate ($CaSO_4$) phases and any other additives. Each of these minerals contributes a large number of peaks to the diffraction pattern, with many overlaps, particularly the well known overlaps between the alite and belite polymorphs. However, thanks to modern implementations of the Reitveld method, it is now possible to untangle the multitude of peaks in a cement diffraction pattern to determine a quantitative analysis of the mineral phases present, with a high degree of accuracy.

Nevertheless, Rietveld analysis can only work well if it starts with a good quality pattern. To have a good diffraction pattern requires contributions from all phases in all orientations, and this implies that many diffracting crystals are presented to the X-ray beam. Figure 3 illustrates the situation where too few crystals have been presented in the sample, and different individual crystal orientations are dominating the diffraction patterns. Figure 3 shows several diffraction patterns that were collected from the same "as-received" cement sample. Each time the sample is presented a different set of individual crystals are contributing intensity to the pattern. To obtain a quality diffraction pattern it is necessary to increase the number of crystals presented.

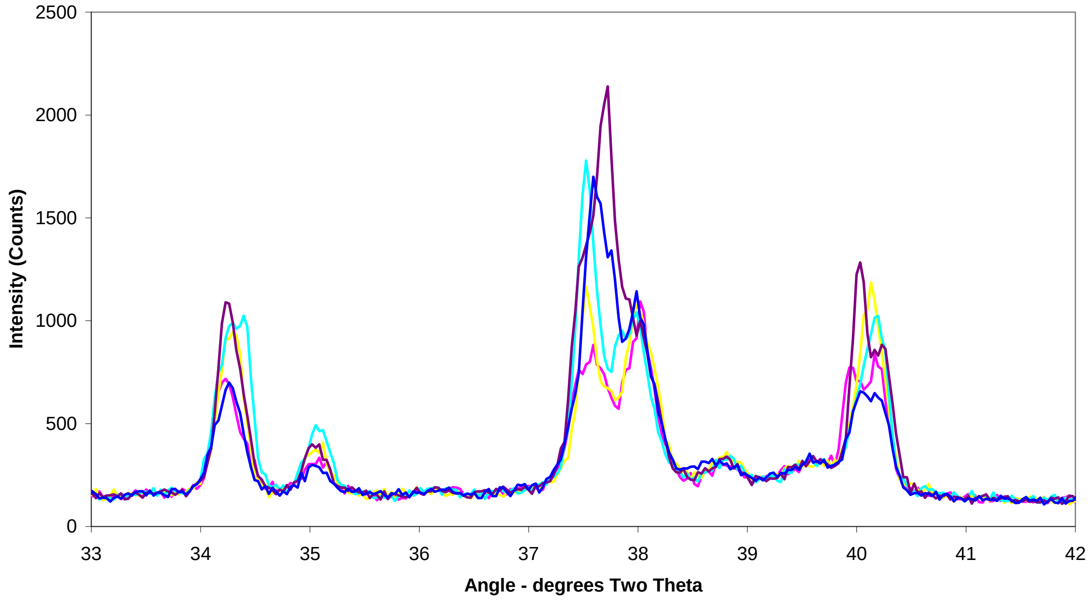

Figure 3: Several diffraction patterns collected from the same sample of as received cement analysed in a single sample holder. The substantial peak variations are due to the

relatively coarse particle sizes in as received cement. In each case different diffracting crystals are dominating the diffraction pattern.

Traditionally the number of crystals presented is increased by fine grinding the sample. This produces many more diffracting crystals, as shown in Table 1 for a sample that has been ground to sub 40µm, 10µm and 1µm. The required particle statistics are discussed in detail in reference 3. Unfortunately the grinding process can cause changes in the sample mineralogy, such as dehydrating the dihydrate ($CaSO_4.2H_2O$) to hemihydrate ($CaSO_4.½H_2O$). These and other effects are discussed in the articles by Füllmann and Walenta and by Enders (Refs 4 and 5). In these articles the authors make reference to the difficulty of obtaining valid and consistent analysis of the hydration states of gypsum using laboratory X-ray diffraction (XRD) analysers. (The interest in gypsum states of course exists because of their significant influence on the setting times of the cement, because these two different forms of $CaSO_4$ have quite distinct properties that influence setting time in different ways.)

Diameter	**40µm**	**10µm**	**1µm**
Crystallites/20mm^3	5.97×10^5	3.82×10^7	3.82×10^{10}
Number of crystallites diffracting	12	760	38,000

Table 1: The number of diffracting crystallites increases as the sample is ground finer (Reference 3).

FCT ACTech's COSMA is designed to optimize the process of continuous on-line analysis of the cement manufacturing process. The analyser was specifically designed for process control in the cement industry. A unique patented sample presentation stage allows for accurate analysis of bulk samples of cement (as-received without further grinding requirement) or of clinker after a simple crushing and grinding to about 50% passing 45µm. The sample presentation stage was developed by FCT in conjunction with the CSIRO Division of Minerals as part of a major research and development program into cement production process control.

A major advantage of the sample presentation stage is to provide for averaging of the multitude of different diffraction conditions that can be found in a cement sample, while removing most of the sample preparation requirement.

By using a sample presentation stage that continuously presents fresh sample to the X-ray beam COSMA is able to easily collect a representative diffraction pattern from as-received cement, avoiding problems from incorrect sample presentation – under grinding, over grinding and preferred orientation. This is clearly illustrated in Figure 4 which shows the diffraction patterns from the same sample that was used to produce Figure 3. In Figure 4 a bulk sample was presented continuously and with continuous presentation any given crystal typically spends no more than one or two seconds in the X-ray beam. Therefore over the accumulation time of a few hundred seconds the sample presentation stage is able to present a few hundred times more crystals than a stationary sample holder, or even a stationary sample holder that is rotating on the spot. Thus COSMA is able to analyse cement as received from the cement mill, with no changes in the mineralogy.

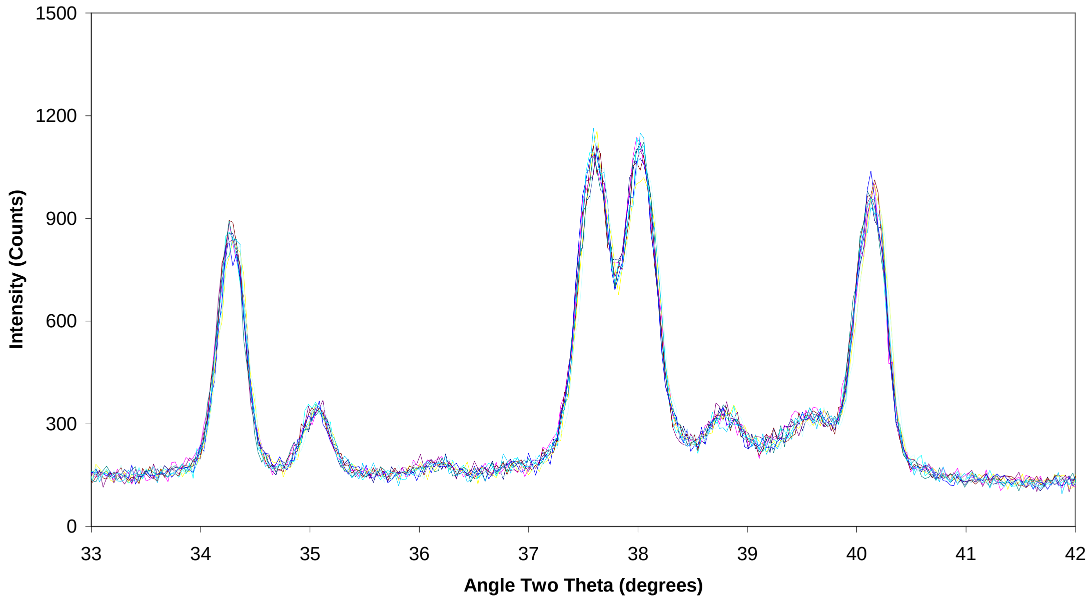

Figure 4: Several diffraction patterns from the same sample presented in the COSMA continuous sample presentation stage. In contrast to Figure 3, the set of diffraction patterns are all fully representative of all orientations of all phases, with only minor statistical variations.

<u>On Site Commissioning</u>

Commissioning the analyser is straightforward and can be completed in a few days because the setup is done in the factory. Each installation requires the services of power, compressed air to assist sample transport, detector gas, cooling water for the X-ray tube and an air conditioned enclosure to maintain the temperature stability of the hardware and electronics. COSMA is designed to be installed out in the cement factory close to the sampling points where it can analyse as-received cement, or clinker that has been crushed and ground to about 50% passing 45µm. If necessary the sample can be easily conveyed up to a few hundred feet using suitable sample transport arrangements.

Typical room enclosures are shown in Figure 5, along with a sample extraction system. The enclosures are adjacent to the cement mill building near to the sampling point. The feedscrew shown at lower left, transfers sample out of a conveyor to drop down into the analyser’s feedhopper. The sample feed rate is about 100-200 grams per minute, with sample being fed continuously and rotated past the X-ray beam by the patented sample presentation stage. After the sample has passed the X-ray beam it is removed and pneumatically conveyed back to a dust collection point in the production process stream.

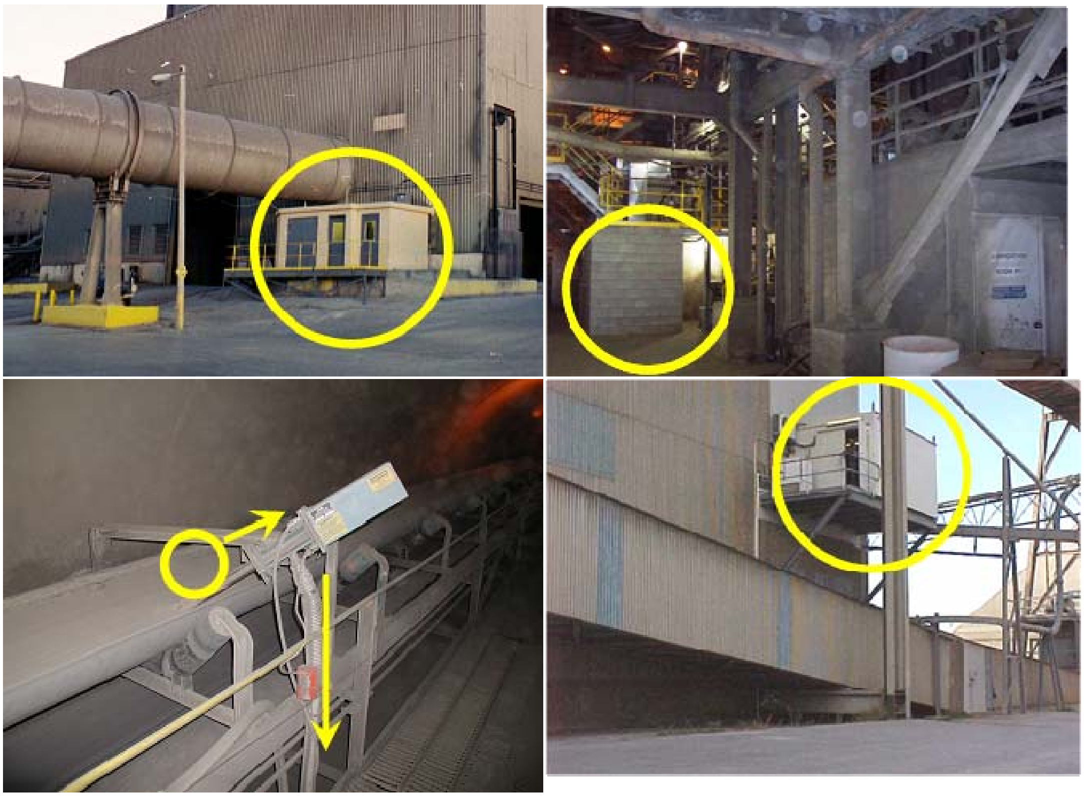

Figure 5: Showing various COSMA enclosures, located near the product stream at the Finish Mill buildings.

In addition to remote control, COSMA has a local operator interface which provides manual or batch analysis of individual samples (Figure 6), even though the analyser is designed for fully automated continuous operation under control of the plant PLC or DCS. Remote service support is available through an internet connection. Typically the system is automatically set to analyse continuously when sample is available, either from the cement mill or from the clinker crushing and grinding unit. Control is specified using the Modbus protocol over Ethernet or over a serial data line. Data is read from COSMA by the plant PLC using Modbus registers and is available for trending on the plants control screens.

Figure 6: COSMA is designed for fully automated operation, but can be used for single sample analysis through the local operator interface. An internet connection allows for remote support and troubleshooting.

Analysis accuracy is assured by precalibration in the factory, using samples of the client's material. This ensures that when COSMA is first started on site the analysis results can immediately be used for process control, without any complicated setup requirements for the analyser or the Rietveld analysis software. Analysis data is then available to the plant every minute while the analyser is running online. The data can be trended to observe and control changes in the process in real time. The data can be averaged over longer time periods to allow for other quality control requirements such as comparison with regular shift samples or daily composite samples. At one plant the confidence gained through making these comparisons has led to all shift sampling being discontinued and COSMA is used for all regular control actions on the cement mill. At that plant full analysis results are also fed back to the on-line raw material control circuit to correct for variations in the mineralogy of the cement, which may come from several different sources.

Conclusion

In summary the continuous analysis of cement process materials has now been proven at a number of installations, and these operations have already been able to take advantage of some of the benefits that continuous quality and process control offers. These benefits include the early detection and correction of process variations, from control of gypsum and limestone addition, to material handling problems such as gypsum and limestone cross contaminations, real time detection of product changes and real time control of free lime excursions.

References

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