RICHARD SIBBICK, GRACE & CO., USA, PROVIDES AN IN-DEPTH LOOK AT WHOLE CLINKER OPTICAL MICROSCOPY.

UNDER THE MICROSCOPE

Chemical additives can improve the efficiency of cement grinding in order to reduce production costs incurred by cement plants. These specialised compounds also serve as quality improvers that deliver significant enhancements to the overall performance of cement.

Previous articles from Grace have highlighted the impact of additives on cement hydration and resulting cement properties and, on the process side, the investigation of additives administered to early open-circuit milling systems through modern day vertical roller mills has been reported. This article highlights whole clinker optical microscopy – a reliable and powerful component of the company's customer service 'toolbox'.

One valuable service is the analysis of cement clinker by optical microscopy. Comparing different clinkers by bulk chemical analysis using X-ray Fluorescence (XRF) and compositional phase analysis by Quantitative X-ray Diffraction (QXRD) alone does not always show obvious or conclusive

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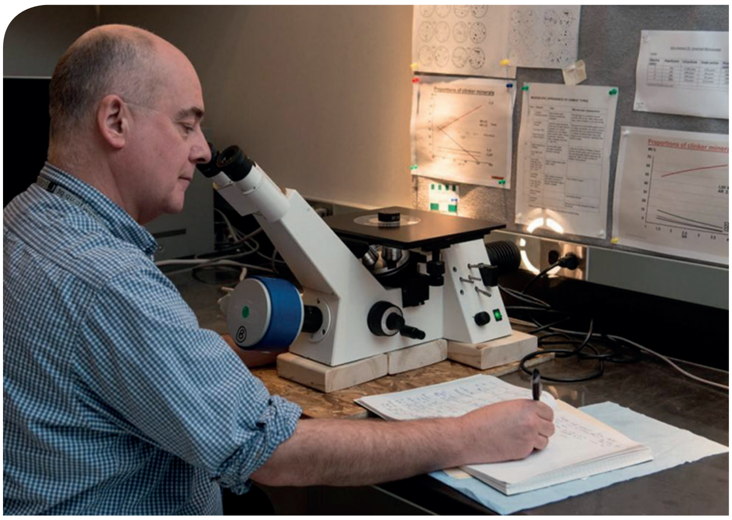


Figure 1. Whole clinker microscopy is typically performed on a standard reflected light microscope.

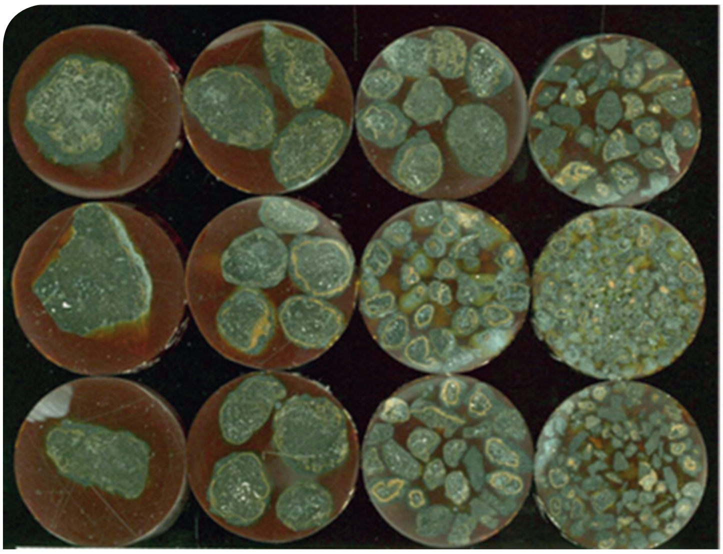


Figure 2. Clinker microscopy is performed using polished samples of the various size nodules found in the whole clinker sample.

effects on cement performance that an end user may observe in either the finished cement or concrete performance. A recurrent cause of this discrepancy is subtle, or gross, microstructural variations between clinkers, often caused by changes in the kiln operational regime or raw feed. The introduction – or increase in the use of – alternative fuels is believed to be one of the most common causes of this variation in clinker quality.

The practical application of optical microscopic assessment of whole Portland cement clinkers was largely developed by Blue Circle Industries in the 1970s in order to determine the extent of microstructural characteristics associated with various kiln-related process issues and was thus used to rectify those problems.

With the continuing improvements in the quantitative analysis of cement clinkers by X-ray Diffraction (Rietveld Analysis) and X-ray Fluorescence Analysis (XRF) combined with lower staffing levels, the use of optical and scanning electron microscopy of cement clinker has become less commonly used in a systematic manner. Likewise, the recent trend for business unit distinction and de-centralisation of technical centres has led to considerable loss of this specialised expertise from even leading cement and admixture suppliers.

Cement clinker has been studied by various microscopic methods, including the production of petrographic thin sections (20 – 25 µm), under the scanning electron microscope (SEM) for many years. However these techniques all have limitations to their application in the general understanding of a clinker's character, making it difficult to use these techniques to compare the quality of a number of clinkers from different sources.

The whole clinker optical microscopy method, exploited by Blue Circle Industries in the UK in the 1970s, is characterised by examining large representative samples of clinker that include the full grading of the clinker sizes produced, as shown in Figure 2. Specimens of nodules and fines representing several size ranges are prepared and studied in detail. Due to the natural variability that occurs within one large representative clinker sample, this method allows one to examine the differences between complete nodule specimens and also any microstructure differences between the core and periphery regions of each nodule specimen prepared. Coupled with knowledge of the feed composition, logged plant information and other relevant background information, it was possible to build an accurate evaluation of each stage of the production process and its impact on the clinker microstructure and quality.

As a result, valid suggestions and corrective actions could be implemented to potentially remedy ongoing clinker issues, further improve clinker quality and reduce production costs. While many other analytical methods used a subset of this knowledge base, it seemed likely that a less detailed approach often overlooks key microstructural features and could potentially lead to false interpretations. The procedure undertaken for this particular investigation is based largely on this clinker analysis method.

The microscopic examination is undertaken on intact nodules of various size fractions that are taken from a larger representative sample. XRF can be used to accurately establish the elemental composition of the clinker and, from that, the potential amounts of the various phases can be calculated using the Bogue analysis. In the case of Bogue analysis, it is well known that because of minor element (Al, Fe, Mg and S) substitution in the crystal lattice of the various phases, and different degrees of combination, the components predicted by this approximation are seldom correct, but are often a reasonable first estimate. X-ray techniques cannot by their very nature identify the microstructural characteristics of cement clinkers, which will further the understanding of a particular clinker's production history and therefore its potential quality.

The use of whole clinker optical microscopy remains an essential tool to better understand a particular production source, and may be used in conjunction with the other analytical techniques available. Moreover, the technique can show a great many microstructural features not always visible using other microscopic methods. These features include porosity changes, colour changes, constituent amounts (qualitative), individual crystals sizes and form, clustering (nest) size and form (alite, belite, periclase, free lime), interstitial amounts and components, degree of crystallinity, minor constituents and many other features. Many of these different features can be observed and may suggest certain process conditions experienced by the particular clinker(s) under examination. This information can thus help resolve a given problem in the plant by changing the feed rate, composition and grinding and/or the kiln variables, such as rotation speed, maximum burning zone temperature, flame position, oxygen level, fan speed, etc.

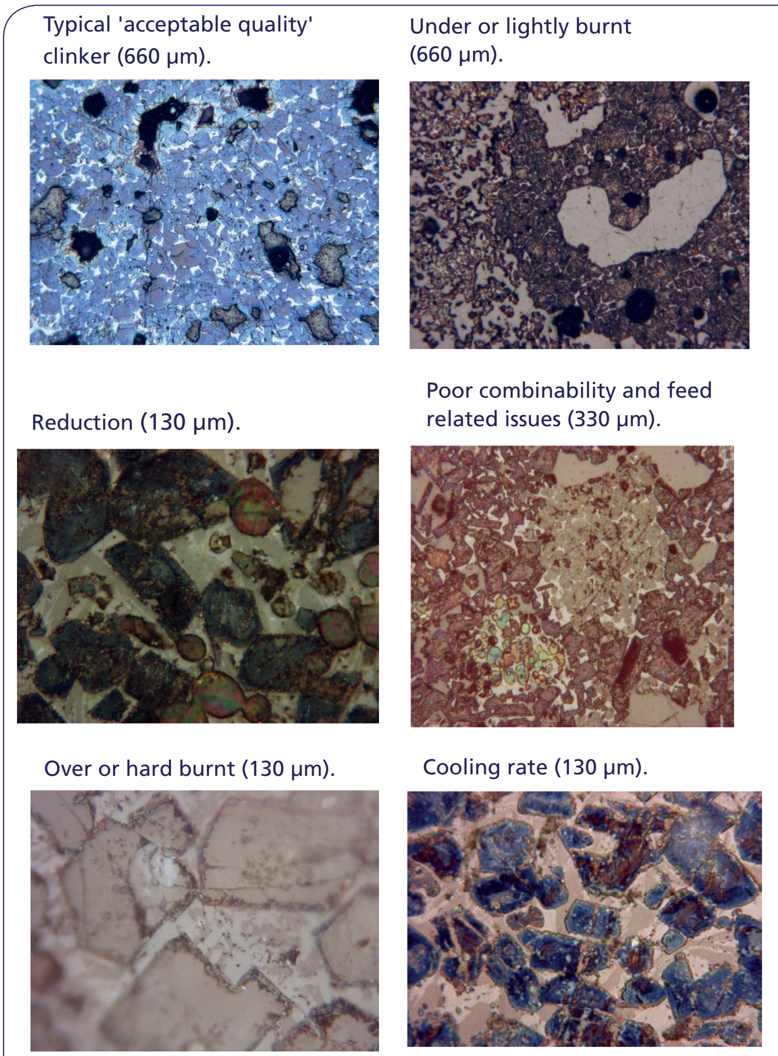


Figure 3. Examples of the microstructural characteristics of clinkers experiencing various process mechanisms. Thorough descriptions of the features typically associated with these various mechanisms were given in Sibbick and Cheung, 2014.[1]

Process conditions affecting cement clinker microstructure

An ongoing survey of many production clinkers has highlighted a series of process issues that were revealed by the whole clinker optical microscopy technique. Typical microstructural characteristics of clinkers experiencing various production issues are summarised in Figure 3. The whole clinker optical microscopy approach used here can establish the presence and extent of these various kiln process conditions or even combinations thereof.

The process issues responsible for the above mentioned features include: challenging raw feed composition and combinability problems, raw feed grinding issues, poor blending, and non-optimum kiln conditions (overloading of the kiln, under-burning, over-burning, cooling rate, slow cooling and reducing conditions), or more often a combination of these.

Any atypical characteristics diverging significantly from this general 'acceptable quality', as shown in Figure 3, can indicate that some process issue may have been overlooked and should be investigated in greater detail. However, all aspects of the clinker morphology must be taken into consideration when making these sorts of determinations, including the degree of the observed variability within the specific clinker under investigation. Two case studies highlighting the types of constructive input afforded by whole clinker optical microscopy are given below.

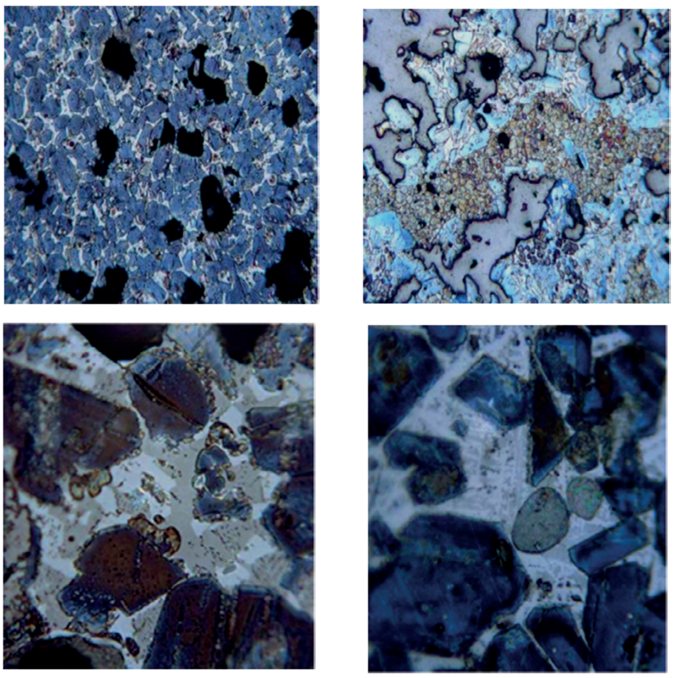
Recent experience has also increasingly shown that evaluating a clinker on a microscopic level can often explain performance responsiveness with chemical additives, thus enabling Grace to assess the most cost-effective additive type for the application required.

Table 1. **Supporting information regarding the clinkers from before and after the fuel change**

	Before fuel change	**After fuel change**
Fuel		
Calorific value (kcal/kg)	4500 – 5000	4000 – 4500
Strength		
3D Strength (MPa)		1 – 2 less
28D Strength (MPa)		3 – 4 less
QXRD		
Alite %	72.6	71.3
Belite %	8.4	7.4
Ferrite %	13.3	12.1
C_3A_cubic %	1.2	1.7
C_3A_ortho %	2.4	3.2
Free lime	0.2	2.0
Periclase %	0.8	1.2
Arcanite %	0.5	0.5
Quartz %	0.3	0.2
Aphthitalite %	0.3	0.4

Before fuel change (660 µm).

After fuel change (660 µm).



(100 µm)
- Well combined.
- Slightly over-burnt.
- Slightly reduced.

(100 µm)
- Poorly combined.
- Under-burnt.
- Strongly reduced.

Figure 4. Shows the differences developed in the clinker microstructure from before to after the fuel change.

Case 1: effect of fuel change

A customer changed the quality and calorific value of the fuel used. This resulted in a reduction in both 3-day and 28-day strengths. Microscopy of the clinkers revealed significant morphological differences. The clinker observation prior to the fuel change was homogeneous and reasonably well combined (maybe even slightly over-burnt), exhibiting a typical clinker appearance, average alite size being 30 – 40 µm, and low free lime content.

The clinker after the fuel change was markedly more heterogeneous, being poorly combined with strong evidence of under burning (less than optimum alite formation and large belite cluster formation), and indications of reducing conditions – all of which negatively impact strength potential, as shown in Figure 4. In this particular case, whole clinker optical microscopy identified that the process grinding and combustion parameters require modification to accommodate the new fuel source and improve clinker burning. Conversely, the associated XRF and QXRD analysis did not highlight any obvious differences or problems.

Case 2: poor performance with chemical grinding aid

A customer's clinker did not exhibit any significant beneficial effects in response to the addition of a new chemical additive (grinding aid). Additionally, the clinker showed no obvious compositional

(XRF and QXRD) features that explained this performance problem. However, microscopic examination of clinker microstructure showed strong evidence for light and under-burning (large fine-sized belite masses), an inability to efficiently combine (abundant, adjacent belite and free-lime clusters) into alite, poor raw feed preparation (abundant coarse randomly shaped belite clusters), and also indications of hard burning, such as an estimated average alite size (EAAS) of 50 – 60 µm.

In this case, the poor performance appeared to be the result of a less than optimum clinker microstructure due to various kiln process factors rather than any incompatibility with the grinding aids being tested.

Conclusion

In summary, whole clinker optical microscopy can often be used to identify subtle process changes in a clinker, which can subsequently be remedied by changes to the kiln or feed set-up, resulting in an improved quality clinker and, most importantly, significant cost savings. Grace maintains this capability in its customer 'toolbox' and this is one of the many technical support services offered to customers.

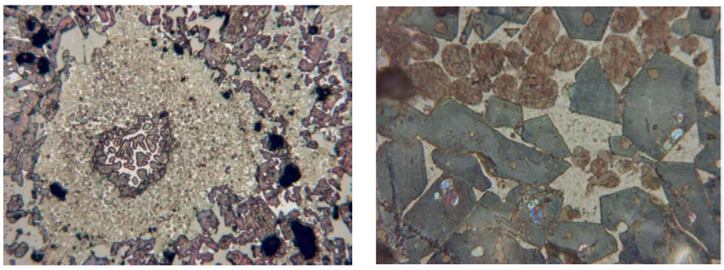


Figure 5. Microstructural characteristics indicative of less than optimal kiln process conditions. Left (600 µm): large adjacent belite and free clusters within a low flux content area. Right (160 µm): coarse sized alite crystals developed in a more flux rich area of the clinker.

Note

The (X µm) number given in the figures represent the various image widths.

Reference

1. SIBBICK, R.G., and CHEUNG, J., Cement Clinker Microscopy as an Aid to Determine Performance Differences in the Presence of Chemical Additives Presented at the 36th *International Cement Microscopy Association (ICMA) conference* in Milan, Italy, April, (2014) http://cemmicro.org/