EVALUATION OF PORTLAND CEMENT CLINKER WITH OPTICAL MICROSCOPY – CASE STUDIES

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Abstract
Clinker microscopy has been a powerful tool for the evaluation of clinker and cement properties for decades. Even in times of fully automated analysis devices like XRF or XRD the optical examination of clinker is still indispensable. Visual, position sensitive observations on clinker granules give additional information on phase distribution and the conditions of the phase formation. Five case studies are presented, showing how optical microscopy of clinker microstructures could help to solve problems of modern cement production.
In three case studies, the parameters of the clinker burning process were not optimal. This had led to reducing burning conditions in the kiln or to poorly burned clinker. Both effects were identified with optical microscopy. The results helped the customers to improve their process and hence their clinker quality.
In two other case studies, the use of secondary material or fuel in the clinker burning process led to the formation of clusters of belite in the clinker. XRD can only find the higher belite and lower alite content of the clinker in such cases. The visual evaluation of the microstructure revealed the respective reasons, enabling the customers to increase the alite content of their clinker.

Keywords: Portland cement clinker, microstructure, case study, burning conditions

Introduction
The quality control in the clinker production process is usually based on X-ray chemical analysis (X-ray fluorescence, XRF). The mineralogical phase composition is derived from the chemistry of the clinker, using stoichiometric approaches of the individual clinker phases. The large scale technical process of clinker burning often leads to deviations of the postulated composition, due to lack of a thermodynamical equilibrium, or to the integration of various minor elements in the clinker minerals. In order to identify the real mineralogical composition, X-ray diffraction (XRD) combined with Rietveld refinement is the analytical method of choice and gains importance in on-line and at-line plant laboratories. However, in many cases this method cannot reveal the cause for observed deviations from the expected “target” composition of the product. In order to investigate the cause and to optimize the production process, the analysis of the clinker microstructure using optical microscopy can be very valuable.
Clinker microscopy is particularly important for investigations which are concerned with the influences of changes in process engineering (e.g. calciner, burner, cooler) or technical parameters (e.g. flame shape, material throughput). Additionally the clinker can be observed under the microscope on possible effects of new raw materials or fuels on the burning process and the clinker properties as well (Campbell, 1999; VDZ, 1965). Generally the comparison of the clinker microstructures before and after the respective changes of the production parameters provides the most significant results. Nevertheless, clinker microscopy is also an important tool for the identification and solution of acute problems in the production process.

Several case studies are presented showing the results of clinker microscopy performed on clinker samples from different European cement plants. Mostly the clinkers have relatively low alite contents despite of raw meal compositions with high lime saturation factor (LSF). Consequently the early compressive strengths of the respective cements were considerably lower than expected. With the help of clinker microscopy the causes could be identified and proposals for the improvement of the clinker quality could be devised.

Sample preparation and analysis

The different clinker samples described here were sampled by the respective producers. One major premise for applicable results is a representative sampling of clinker. Therefore, considering the substantial mass flow in the clinker production process, the sampling has to be carried out accurately.
For the examination of the clinker samples with optical microscopy, 4 granules with diameters of about 1 cm of each unprocessed sample were embedded in low viscosity epoxy resin under vacuum. Additionally, representative subsamples with grain sizes of 2 - 4 mm were obtained by crushing the clinker samples in a jaw crusher and sieving the crushed material. These subsamples were likewise embedded in epoxy resin under vacuum. After curing, polished sections of the embedded samples were produced. The final polishing step was performed with an anhydrous suspension of diamonds with a maximum grain size of 1 µm. The polished sections were etched with a 10 % KOH solution as well as an alcoholic dimethyl ammonium citrate (DAC) solution for several seconds, respectively, and than investigated with an optical microscope under reflected light. The etching procedure enables the distinction of the different clinker phases (alite/C_3S Ca_3SiO_5; belite/C_2S Ca_2SiO_4; C_3A $Ca_3Al_2O_6$; brownmillerite/C_4AF $Ca_4(Al,Fe)O_5$; free lime CaO) under the microscope (VDZ, 1965). While the Brownmillerite (C_4AF) is recognizable due to its strong reflectivity without etching, the other three main clinker phases look very similar under reflected light. The KOH solution causes a discolouration of the C_3A from a light gray to a darker gray or brown. The DAC solution etches the surface of alite crystals which produces an apparent sharp dark line around the crystals. A colour change of alite from light grey to a darker grey or brown is common. Belite is slightly etched structurally and slightly changes its colour from light grey to a darker grey.

Results - findings of the case studies

Effects of fineness and homogeneity

In the first case study two clinker samples which had been produced with waste foundry sand as a raw meal component were analysed under the microscope. In the first case the sand was used in an unground state, in the second case it had been ground beforehand. The samples were compared to evaluate the influence of the sand´s fineness on the microstructure.
The clinker sample which had been burned with the untreated sand contained a high amount of belite clusters with diameters of up to several tenth of a mm. Many of the clusters enclose one or several central pores (Figure 1). These belite clusters typically occur when the raw meal contains large grains of SiO_2-rich materials (e. g. VDZ, 1965). The grains cause enrichments of SiO_2 on the microscopic scale. The silicon ions are relatively mobile during the clinker burning process and move from the SiO_2-rich grains into the CaO-rich surroundings, where belite forms. The local depletion of CaO inhibits the further reaction to alite. The process leaves a pore in the centre of the former siliceous grain which has not necessarily the shape or size of the former grain (Maki et al., 1995).

The clinker sample burned from the raw meal mix with ground waste foundry sand contained a much smaller amount of large belite clusters with central pores. Instead, the occurrence of belite distributed homogeneously throughout the microstructure was higher in this sample.
The observations show that the microstructure of Portland cement clinker strongly depends on the fineness of the raw meal. Large grains can cause inhomogeneities in the clinker. In this case the high amount of belite clusters could also have an impact on the grindability of the clinker.

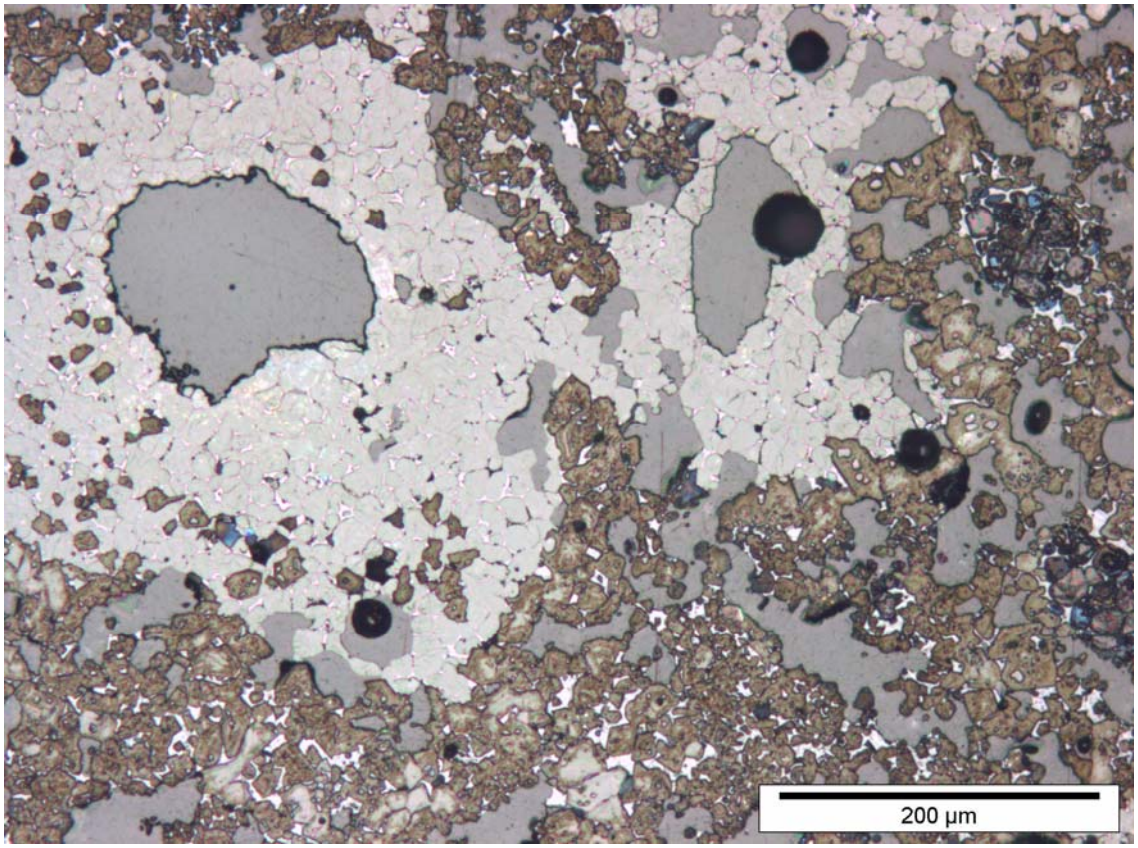

Figure 1: Belite clusters with central pores

Residence time at sintering temperature

In a second case study a customer reported strongly varying alite and free lime contents of the clinker produced in one kiln line. Several of the investigated clinker samples partly consisted of granules showing a phase assemblage of mostly alite and belite with crystal sizes of more than 10 µm. The porosity of this material was relatively low. This appearance is characteristic of well burned clinker (Figure 2). Nevertheless, a significant amount of the samples was composed of grains with very inhomogeneously distributed free lime, belite and interstitial mass phases. Belite and free lime occurred in close vicinity. Alite was relatively rare in these granules. The crystal sizes of all main phases were mostly below 10 µm and the porosity was very high and unevenly distributed (Figure 3). These are typical characteristics of poorly burned clinker (VDZ, 1965; Campbell, 1999). Poorly burned clinker results from insufficient burning temperatures or a too short period of time in which the material stays at sintering temperatures. Under these conditions the reaction of belite and free lime to alite is too slow or disrupted too early to form a sufficient amount of alite. Significant fractions of such material in the clinker causes a reduction of the alite content compared to the potential alite content

calculated from the raw meal chemistry. The high amounts of free lime in the poorly burned clinker additionally could affect the soundness of the cement produced with this clinker.

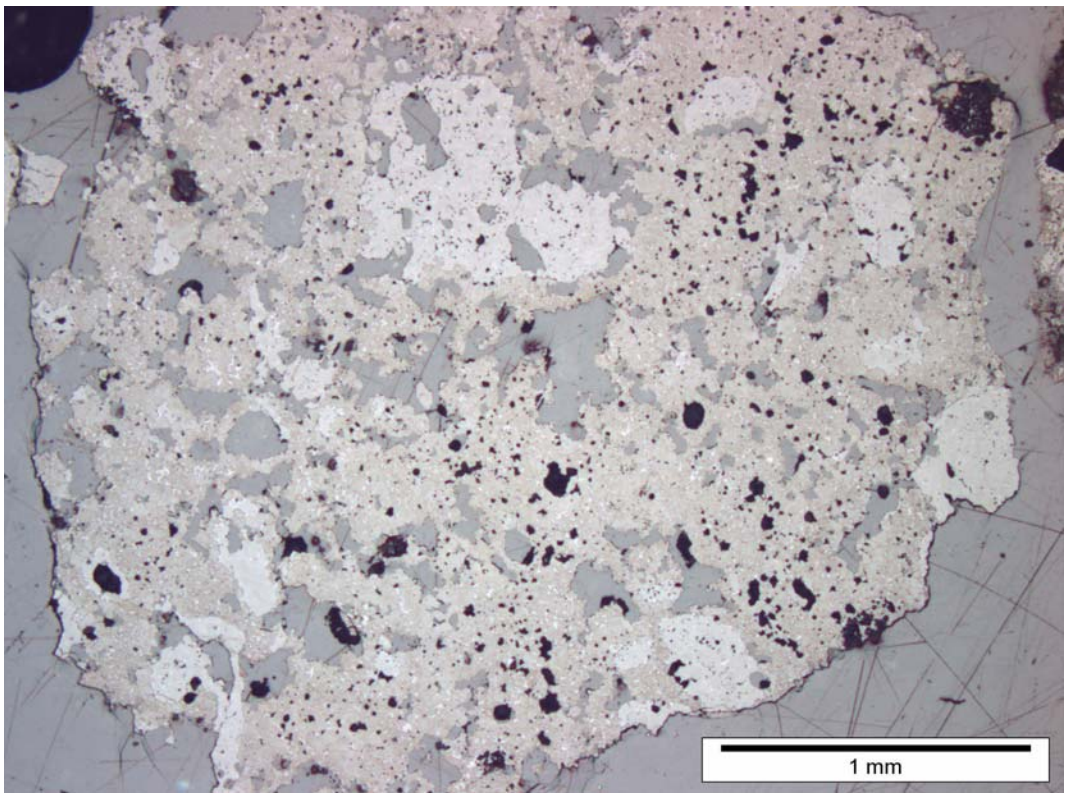

Figure 2: Well burned clinker with typical phase assemblage and few belite clusters

Apart from the extreme appearances, intermediate clinker grains regarding the burning grade (contents of alite, belite and free lime, porosity and homogeneity of the microstructure) were observed in the clinker samples (Figure 4).

The presence of alite-rich grains in the sample shows that the maximum temperature to which the material was exposed during the clinker burning process sufficed to enable the reaction of belite and free lime to form high alite contents. Therefore the poorly burned material cannot be ascribed to insufficient burning temperatures in the kiln.

Short-term irregularities in the flame control (flame shape or length, flame temperature) are one main cause for such poorly burned clinker mixed with well burned clinker. These conditions lead to small-scale variations in the maximum temperatures and in the residence time at maximum temperature of the kiln feed, resulting in a product with strongly differing burning grades.

The mass flow rate is another important factor. A high clinker bed in the kiln can lead to shielding effects, reducing the heat transfer from the flame into the centre of the moving clinker layer. At the same time the heat transfer into the material exposed to the kiln atmosphere induces high burning grades in this fraction of the material.

As a result of the observations the customer was advised to control and decrease the mass flow rate of the kiln feed and to stabilize the flame shape, length and temperature.

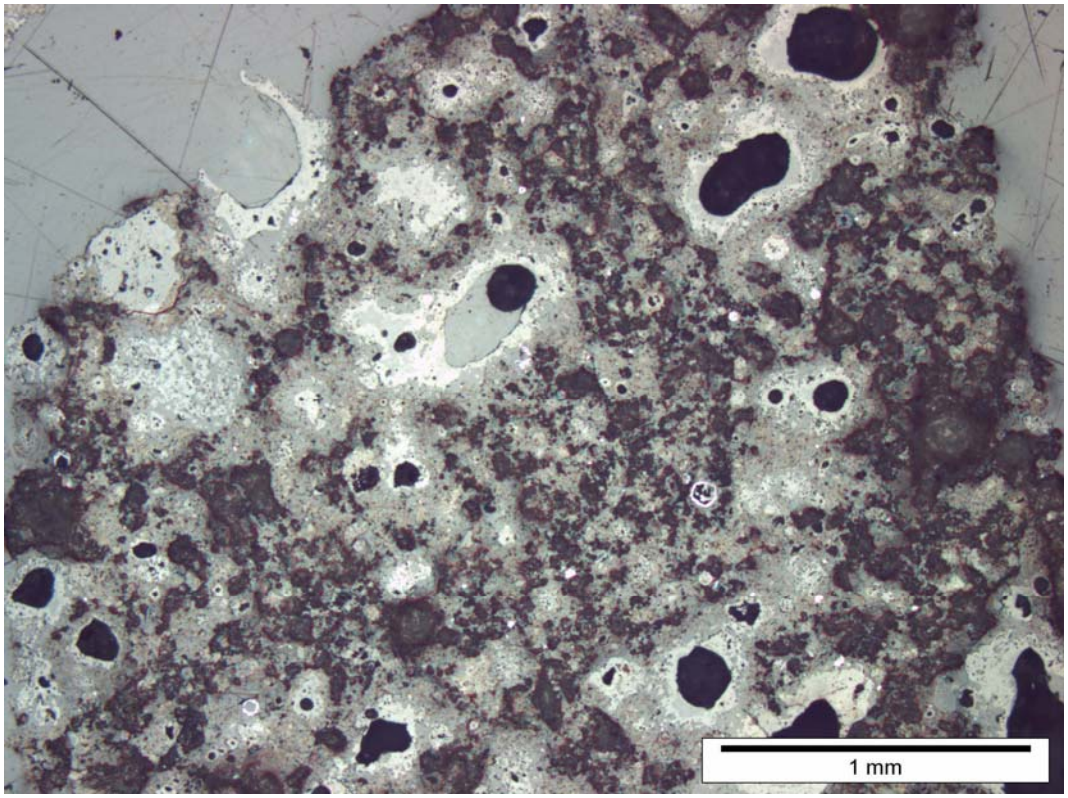

Figure 3: Belit clusters (light grey) and free lime (dark grey) in a poorly burned clinker grain

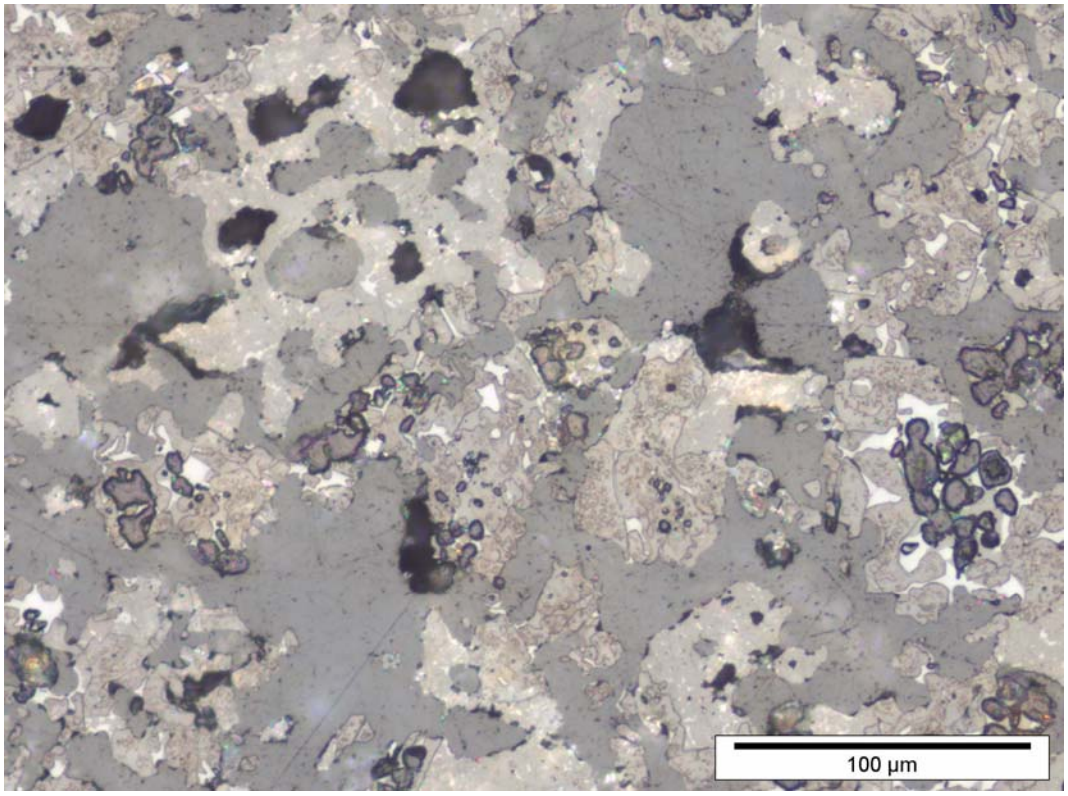

Figure 4: Porous clinker resulting from intermediate burning

Formation of large clinker granules

In a further case study, a customer had observed changes in the clinker properties. The cement produced from the clinker exhibited a lower strength than usual. To achieve the normal strength, the clinker had to be produced with a higher lime saturation factor (LSF) and ground to a higher fineness. The customer also reported the formation of large clinker granules with diameters of 5 cm and more in the clinker burning process.

Several clinker samples were analysed microscopically. The findings were similar to those of the case study described above. Well burned clinker coexisted with poorly burned clinker.

Supplementary chemical analyses of hot meal samples taken from the process found significant amounts of chloride and relatively high amounts of sulfate and alkalis. The clinker samples themselves only contained minor amounts of chloride and common amouts of sulphate and alkalis. Chloride, sulphate, sodium and potassium have relatively high vapour pressures at temperatures typical for the clinker burning process. They evaporate in high temperature areas, are transported with the gas stream counterflowing the material stream and condensate at lower temperatures on the kiln feed, building up a cycle (e. g. Locher, 2005). Therefore there are certain areas in the kiln where the kiln feed contains higher amounts of the volatile substances than the clinker leaving the process. Coincidently these substances can cause, in certain concentrations, the formation of mostly needle-shaped phases (Sylla, 1974), which promote the growth of large hot meal granules. Depending on the temperature profile in the kiln and the mass flow rate in the process, the centres of these large grains might not reach sintering temperature or remain too short in the sintering zone, leaving the kiln in a poorly burned state while the outer layers of the granules as well as small granules are well burned.

To avoid the formation of large hot meal granules, the customer was advised to reduce the amount of volatile substances in the kiln. This could be done by the reduction of the amount of volatile-rich materials in the raw meal or in the fuel mix. Another approach is the extraction of volatile rich dust from the process using a so called bypass.

Influence of phosphate

In a fourth case study three clinker samples taken by a customer over a time range of two years were characterized with clinker microscopy.

All three samples mainly consisted of the four clinker phases (alite, belite, C_3A, brownmillerite) with certain amounts of free lime. Free lime formed clusters of various sizes, while belite occurred in clusters as well as finely distributed in the matrix. The most outstanding features of two of the samples were clusters of belite crystals mixed with free lime crystals (Figure 5). These clusters were found in the rims of granules as well as in their centers. The direct contact of belite and free lime in an otherwise well burned clinker is unusual. Since these clusters were surrounded by alite, the temperatures of the clinker burning process must have been sufficiently high. Supplemantary analyses under a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) detected significant amounts of phosphor in the belite crystals of these clusters. Phosphor can stabilize belite due to the formation of a solid solution of C_2S and C_3P ($3CaO*P_2O_5$). This phase does not react with CaO to alite at usual sintering temperatures (Puntke and Schneider, 2008).

One of the clinkers contained a phosphor-induced belite-free lime-cluster with a diameter of about 2 mm, in the center of which no belite or free lime could be identified microscopically. EDX analyses under a SEM identified these phases as calcium phosphate (probably $Ca_3[PO_4]_2$) and an alkali bearing calcium phosphate.

The customer had used a phosphate-rich secondary fuel. Consequently, the highly inhomogeneous distribution of phosphor with high concentrations in isolated areas, causing the formation of the

belite/free lime-clusters, could be attributed to large grains of phosphor-rich ash. These particles were integrated in the clinker granules. The formation of the clusters lowered the alite content and raised the free lime content, thereby possibly affecting the strength development and the soundness of the cement produced from this clinker. These effects can be expected to be less pronounced, when the phosphor is more homogeneously distributed in the clinker, even at the same total amount of phosphate in the fuel. The phosphate effect is usually uncritical with phosphate contents lower than 1 % by mass in a clinker. Therefore, the customer was advised to use the phosphate bearing fuel in a more finely processed state and/or in lower amounts.

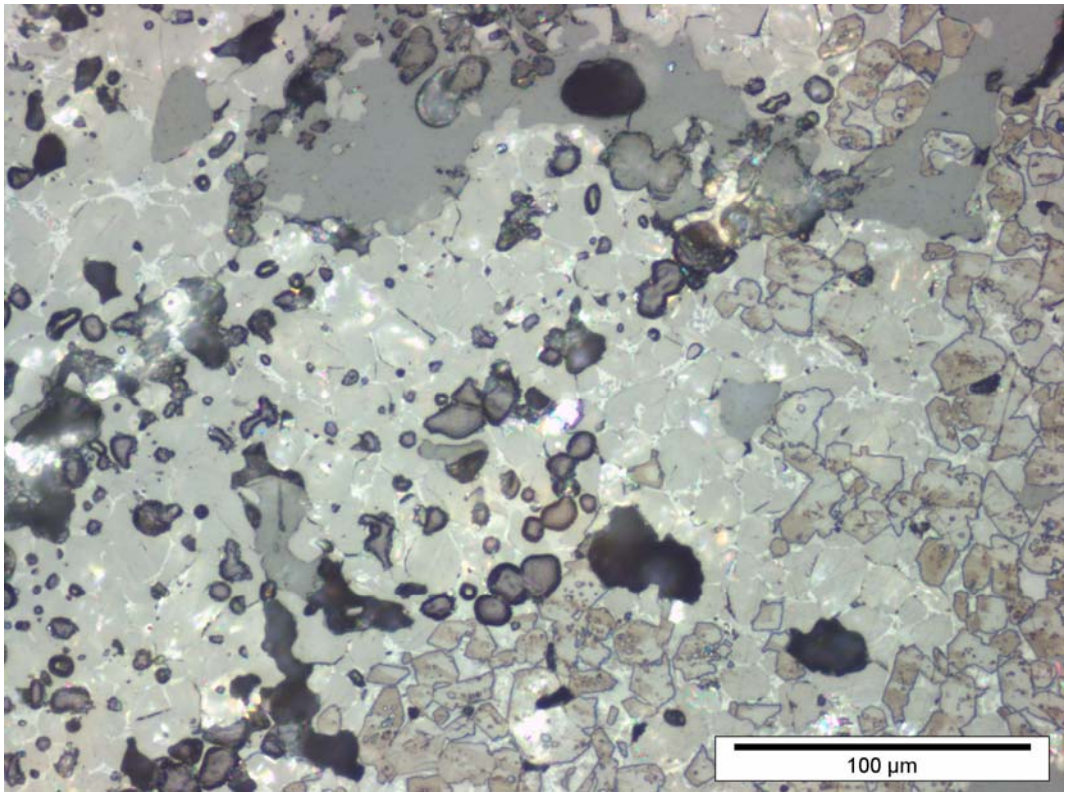

Figure 5: Belite enriched in phosphate (light grey), interspersed with fine grained free lime (dark grey)

Reducing burning conditions

In a fifth case study, a customer reported varying early strengths of his Portland cements. To clarify the causes, two different clinker samples were characterized microscopically and with XRF and XRD. One of the clinker samples represented a cement with usual high early strength, while the other one represented a cement with a low early strength.

The chemical analysis showed very similar composition of the two samples, while the phase composition according to XRD revealed about 4 % by mass lower alite and about 6.5 % by mass higher belite contents in the low early strength clinker compared to the other sample. Microscopical analysis of both materials identified similar burning grades in both samples, but also revealed typical indicators for reducing burning conditions in both clinker samples. These indicators occurred significantly more often in the low early strength clinker.

The most typical sign for reducing burning conditions is the decomposition of alite to belite and free lime. This can be explained by the incorporation of Fe^{2+} ions in the crystal structure of alite. Fe^{2+} iron only occur under reducing conditions in the kiln. When the clinker is subsequently exposed to oxidizing conditions the iron in the alite crystals oxidizes to Fe^{3+}, which has a smaller ionic radius.

This destabilizes the crystal structure of alite and induces its (partial) decomposition (e. g. Sylla, 1981). The decomposition process is often restricted to small volumes along crystallographic preferred orientations. In some cases the decomposition starts from the rim of the alite crystals and proceeds towards the centre. Both effects were observed in the two clinker samples (Figure 6).

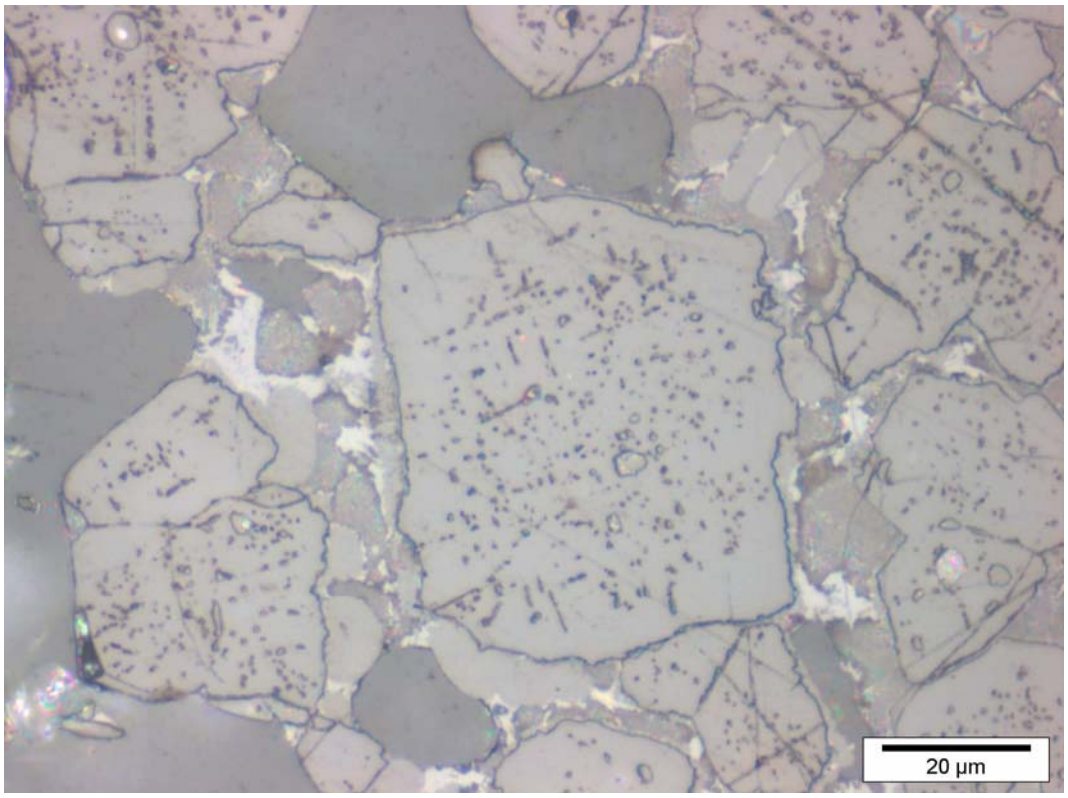

Figure 6: Alite burned in reducing atmosphere, showing partly decomposition to belite and free lime along crystallographic preferred orientations

Under strongly reducing conditions, iron can be reduced to or kept as metallic iron (e. g. Sylla 1981). In both clinker samples, drop-shaped particles of metallic iron could be observed. Very small particles of metallic iron were even enclosed in alite crystals. The interstitial phases in these areas completely consisted of C_3A, so no iron was locally available for the formation of Brownmillerite (Figure 7).
The clinker quality can be affected by reducing conditions in several ways. Firstly, the destabilization of alite leads to lower alite and higher free lime contents, thereby possibly affecting the strength development and the soundness of the cement produced from this clinker. Secondly, the decomposition of alite can lead to belite in the γ-modification, which does not show hydraulic properties at all and enhances the decrease of strength of the cement. Thirdly, Fe^{2+} or even metallic iron in the cement can promote brown discolourations on the surface of concrete.
Therefore the prevention of reducing conditions in the kiln is important. They are mainly caused by smoldering fuel particles falling on the clinker bed and being buried due to the rotation of the kiln. The reducing conditions are restricted to the immediate neighbourhood of these particles. To avoid this, the fuel particles have to burn out completely before falling on the clinker bed. This problem can be approached in several ways. The fuel can be comminuted to a higher fineness, the shape and temperature of the flame can be modified or additional oxygen can be introduced into the flame.

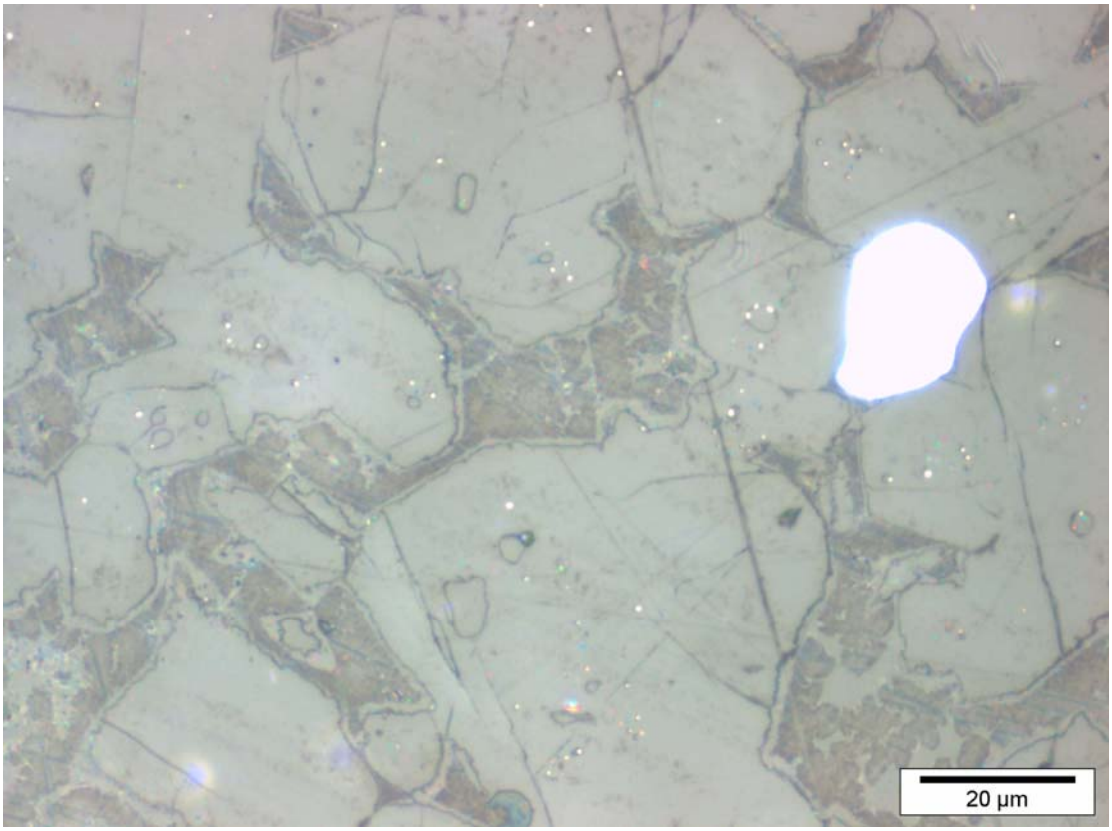

Figure 7: Metallic iron (white) forming a 20 µm large droplet and small inclusions (< 1 µm) in alite crystals

Conclusion - practical use of clinker microscopy

The optical microscope analysis of the clinker microstructure can supply useful information for process optimization, which cannot be attained alone by integral testing methods on bulk samples, like XRF or XRD. In particular with the comparison of the „before/after" quality of the product, influences of changes in material or process engineering could be described, and references to possible corrections of the process could be given. So if modifications of the clinker burning process are projected, comprehensive retention samples of uncrushed clinker should be taken and stored. This can be the basis of well founded analyses if any changes appear in the product quality.

The analytical method of optical microscopy of the clinker microstructure is complex and time consuming, and it requires laboratory staff with experience in preparation and interpretating the findings. Nevertheless, if information can be obtained that helps to enhance the quality of a product mass flow of up to 10,000 tons per day, the effort will be worthwile. Usually it is not necessary to have the expertise available in each cement plant. Consulting a central laboratory or research centre will be the most efficient strategy.

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