Evaluation of portland cement clinker with optical microscopy - case studies III

Matthias Böhm*, Klaus Lipus

VDZ gGmbH, Research Institute of the Cement Industry, Düsseldorf, Germany.

* Matthias.Boehm@vdz-online.de

Abstract

Clinker microscopy is a powerful tool for the evaluation of clinker and cement properties. Microstructural investigations yield important information on phase distribution and the conditions of the phase formation. The correct understanding of clinker microstructure is crucial for an accurate evaluation of raw material, fuel or process parameters. Two case studies on clinker samples are presented, in which individual granules with unusual microstructure characteristics were observed.

In the first case study, the clinker contained a granule the centre of which mainly consisted of belite crystals in direct contact with free lime crystals. Additionally several alite crystals that had partially decomposed to belite and free lime from the rim inwards were observed in the granule centre. EDX measurements, element mapping and the interpretation of the microstructure showed that an accumulation of barium, probably introduced into the kiln as baryte, was the cause of the observed local phenomena.

In the second case study, granules with domains containing elemental iron were observed. Additionally these domains contained alite, high amounts of C_3A, no belite and no C_4AF. The iron was intergrown with free lime. Estimations based upon the surface area ratio of the phases in the intergrowths show that C_4AF is probably the compound from which the intergrowths formed after reduction of ferric iron to elemental iron.

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

I. Introduction

The use of alternative fuels and raw materials (AFR) for the production of Portland cement clinker has gained more and more importance over the last decades and this trend continues. These materials contribute materially to the formation of the clinker phases and help to save fossil fuels and natural raw materials. The use of AFR can influence the clinker properties. Many of the effects can be observed in the clinker microstructure.

Therefore clinker microscopy is also gaining importance as an analytical method, withstanding the trend to automatable, quantitative methods like X-ray fluorescence (XRF) or X-ray diffraction (XRD). Microscopy can provide information on the phase distribution and the conditions of the phase formation, which are important for the evaluation not only of the effects of AFR, but also of fossil fuels and natural raw materials.

The correct understanding of the clinker microstructure is crucial for an accurate evaluation of raw material, fuel or process parameters. This requires extensive experience from the microscopist. Case studies on rare or previously undescribed features help microscopists to broaden their experience backgound.

Selected results of two microscopic investigations on clinker samples are presented here, performed for cement plants for the evaluation of burning conditions, especially for the confirmation of the absence or presence of signs for reducing burning conditions. In the respective clinker samples unusual microstructural characteristics were observed and interpreted, partly with additional information from scanning electron microscopy.

II. Sample preparation and analysis

For the examination of the clinker samples with optical microscopy, representative subsamples with a grain size of 2 - 4 mm were obtained by crushing the clinker sample in a jaw crusher and sieving the crushed material. The subsamples were embedded in epoxy resin under vacuum. After curing, polished sections of the embedded samples were produced. 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 then investigated with an optical microscope (Zeiss Axioplan) 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/$Ca_2(Al,Fe)O_5$; free lime/CaO) under the microscope. 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 grey to a darker grey 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.

Additionally to light microscopy, the polished section from case study 1 was analysed with a scanning electron microscope (Philips ESEM XL30 FEG) with the possibility for energy dispersive X-ray (EDX) analysis. EDX analyses were carried out in the form of spot analyses and in the form of element mappings.

III. Results of case study 1

In this case study a clinker sample was analysed to estimate the effects of different fuels on the clinker properties. In general the clinker sample was well burned and did not show unusual phases or microstructural features.

However, one single clinker granule in the polished section consisted mainly of belite, free lime and ground mass (C_3A, C_4AF) with a low amount of alite crystals. The alite crystals were surrounded by a symplectite of belite (belite I in Figures 1 and 2) and fine grained free lime crystals (free lime I in Figures 1 and 2). The free lime crystals were often oriented towards the alite crystals. The symplectites formed a layer of up to 20 μm thickness. Many symplectites did not contain cores of alite. Beside these symplectites with and without alite cores, the granule consisted of a mixture of coarse grained belite (belite II in Figures 1 and 2) and free lime crystals (free lime II in Figures 1 and 2).

In usual Portland cement clinker the direct contact of belite and free lime occurs only as a result of high concentrations of phosphorous (e.g. Puntke, Schneider, 2005), of alite decomposition due to reducing burning conditions (VDZ, 1965; Böhm, 2011) or in poorly burned material. Poor burning leads to crystal sizes below 10 μm and high porosity (VDZ, 1965; Campbell, 1999; Böhm, Pierkes, 2009). Both features were not found here. Additionally large alite crystals (Figure 1) prove that the material was exposed to conditions sufficient for alite formation. Phosphorous can stabilise belite, preventing the formation of alite and leading to a mixture of coarse grained belite and free lime (Puntke, Schneider, 2005; Böhm, Pierkes, 2009). However, symplectites of belite and free lime as they were observed here (Figure 1) usually do not occur in connection with phosphorus.

The symplectites of belite and free lime surrounding alite crystals and the orientation of the elongated free lime crystals pointing towards the alite crystals indicate the (partial) breakdown of alite. The symplectites with and without alite cores probably formed as pseudomorphs after alite. The most common cause for the breakdown of alite in modern Portland cement clinker is the occurrence of local reducing conditions in the kiln feed, caused by smouldering particles of AFR. This can lead to symplectites of belite and free lime as in Figure 1. However, reducing conditions do not prevent the formation of alite as indicated by the coarse grained mixture of belite and free lime crystals around the symplectites.

To clarify the cause for the formation and subsequent partial breakdown of alite while at the same time the formation of alite was prevented in the vicinity, the clinker granule was analysed using SEM and EDX analyses. The measurements revealed unusually high concentrations of barium in the clinker granule (Table 1). Alite contained less than 2 mass % of barium. The belite crystals in the symplectites (belite I) contained about 7 mass % of barium, whereas the belite crystals mixed with coarse grained free lime (belite II) contained about 10 mass % of barium. The barium distribution between alite and the two populations of belite is also illustrated in the element maps in Figure 2.

The different barium contents and the microstructural features lead to the following interpretation. The high barium content in the belite II-crystals prevented the formation of alite and led to a microstructure comparable to that caused by high concentrations of phosphorous. The concentrations of barium in the remaining alite crystals was not high enough to prevent the formation of alite at sintering temperatures or the breakdown of alite to belite and free lime during cooling. However, in some alite crystals the barium concentration was low enough to allow the formation of alite at sintering conditions, but high enough to destabilise the crystal structure, leading to its disintegration during cooling and the formation of symplectites of belite I and free lime. This process either led to the breakdown of complete alite crystals or only of the outer rims, indicating zonation in the original alite crystals with increasing barium contents from core to rim.

It remains unclear if the inhomogeneous distribution of barium is the consequence of the inhomogeneous distribution of the element in its source. Another plausible explanation would be that the alite crystals selectively incorporated lower amounts

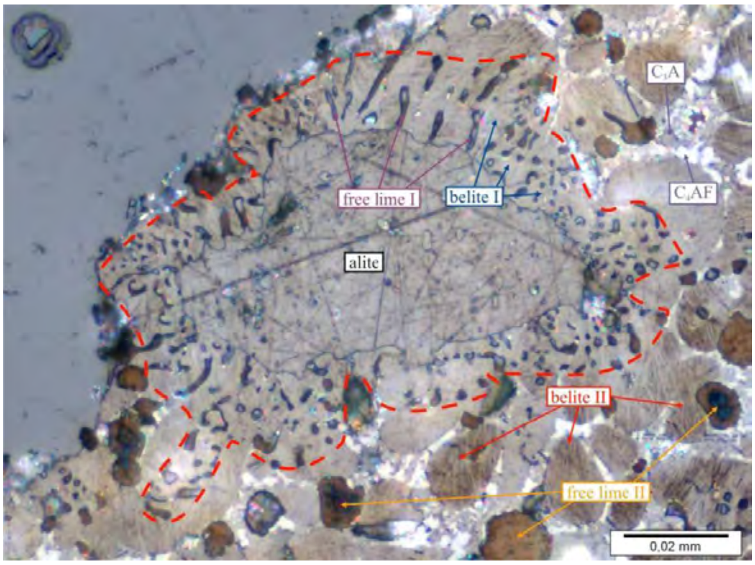

Figure 1: Reflected light micrograph of clinker; alite directly surrounded by a symplectite of free lime crystals often oriented towards alite (free lime I) and belite crystals (belite I), itself surrounded by a mixture of coarse round free lime crystals (free lime II) and belite (belite II); outer rim of symplectite marked with dashed red line.

of barium at the beginning of their formation at lower temperatures and increased the incorporated amount in outer zones formed later and therefore at higher temperatures. The observation that zones containing higher barium concentrations disintegrated during cooling indicates that the amount of barium, which can be integrated into the alite crystal structure, increases with increasing temperature.

The granule described here was the only one in the polished section showing microstructural features influenced by barium. The source for barium was therefore an exceptional compound in the raw materials or fuels used. The most probable source is a crystal of baryte (BaSO4), which can be found in the limestone formations used in the cement plant in which the clinker was produced.

The average amount of barium in cements is 280 mg/kg. It replaces Ca in all clinker phases except C_4AF (Bhatty, 1995). It can decrease the clinkerisation temperature, improve the mineralogical composition and increase cement strength (Bhatty, 1995). However, most studies worked with smaller concentrations of barium than found in the clinker granule described here (e.g. Bhatty, 2006).

IV. Results of case study 2

Also in this case study a clinker sample was analysed to estimate the effects of different fuels on the clinker properties. The clinker sample was well burned and mostly did not show unusual phases or microstructural features.

However, in some granule fragments in the polished section alite crystals partially decomposed to belite and free lime and/or C_4AF along crystallographic preferred orientations. In some granule fragments alite crystals partially decomposed to symplectites of belite and free lime. Both microstructural features indicate reducing burning conditions (VDZ, 1965; Böhm, Pierkes, 2009; Böhm,

Table 1: EDX measurements of the composition of alite, belite I (crystals close to alite and in contact with fine grained free lime), and belite II (crystals remote from alite and in contact with coarse grained free lime).

Oxide	alite (3 measurements)	belite I (3 measurements)	belite II (7 measurements)
CaO	66.4 ± 0.2	59.0 ± 2.1	55.4 ± 1.5
SiO_2	26.4 ± 0.2	28.8 ± 2.7	30.3 ± 1.2
BaO	1.3 ± 0.7	6.8 ± 0.2	9.8 ± 1.6
Al_2O_3	2.5 ± 0.1	2.5 ± 0.5	2.0 ± 0.4
Fe_2O_3	0.8 ± 0.1	1.1 ± 0.1	1.0 ± 0.4
MgO	1.6 ± 0.4	0.7 ± 0.5	0.4 ± 0.2
K_2O	0.3 ± 0.1	0.7 ± 0.1	0.7 ± 0.1
Na_2O	0.7 ± 0.5	0.4 ± 0.1	0.3 ± 0.1

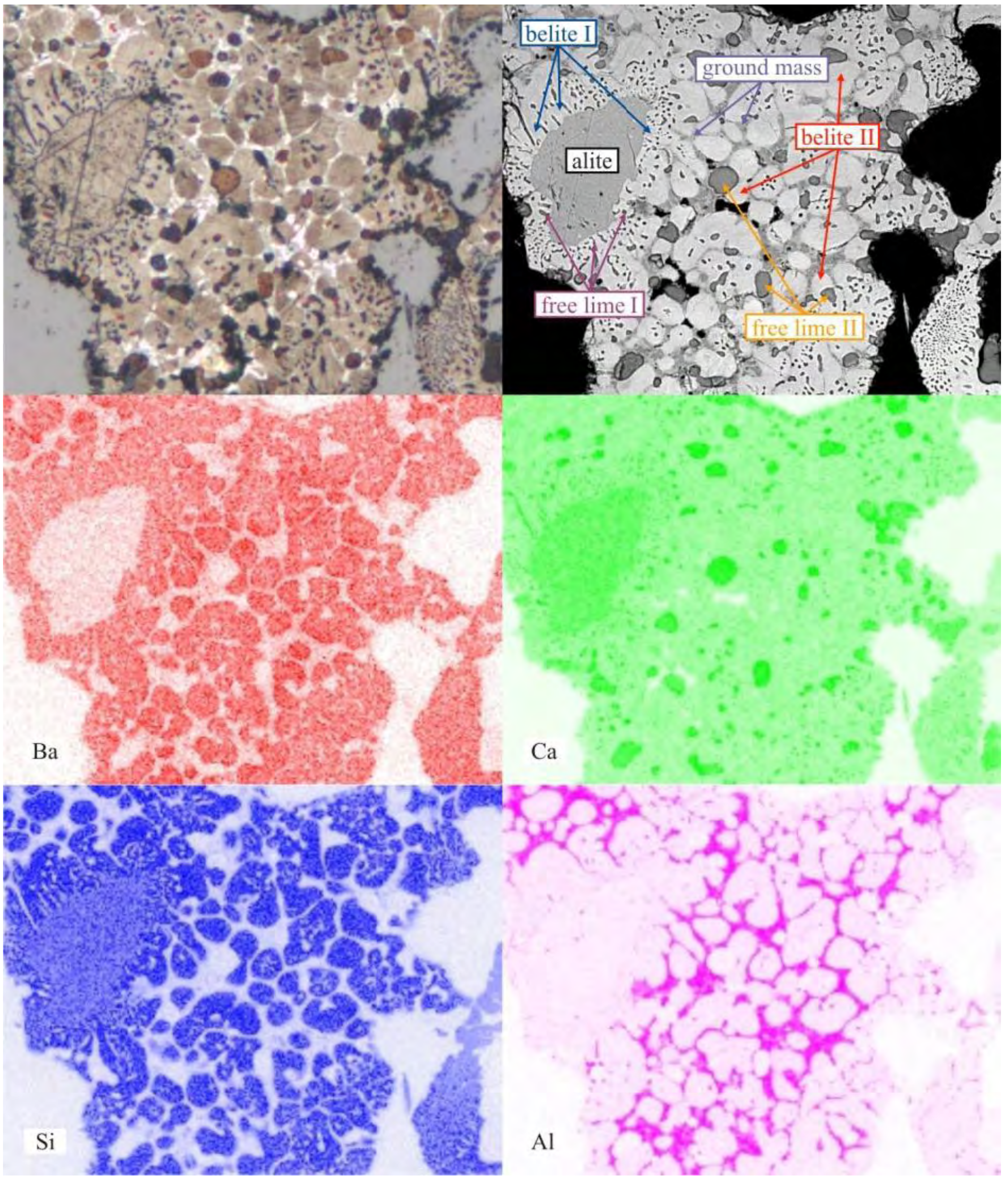

Figure 2: Reflected light (top left) and SEM micrograph (top right) of clinker; elemental maps (Ba mid left, Ca mid right, Si bottom left, Al bottom right) of alite directly surrounded symplectitic arrangement of free lime and belite, itself surrounded by a mixture of coarse free lime and belite; width of each image 235 µm.

2011). The decomposition of alite is caused by the incorporation of Fe^{2+} ions in the crystal structure of alite. The ions form under reducing conditions in the kiln and they destabilise the crystal structure of alite (e.g. Sylla, 1981).

Additionally several clinker granule fragments contained elemental iron particles forming symplectites with free lime crystals (Figure 3). These particles also contained alite, partially decomposed to fine grained symplectites of belite and free lime, as well as belite and C_3A, while C_4AF was not preserved. In these clinker particles belite and C_3A were hard to discern with the etching procedure described above (Figure 3).

Iron particles can form under strongly reducing conditions, but they are usually not intergrown with free lime (e.g. Pierkes, Böhm, 2009). The recurring symplectitic structure of iron and free lime indicates an equally recurring precursor phase containing CaO as well as Fe. The symplectites were xenomorph and seem to form, together with the areas consisting of C_3A and belite, a groundmass in which alite crystals are embedded.

Probably C_4AF was the precursor phase for the symplectites. It must have formed before the material was exposed to strongly reducing conditions, which led to the conversion of ferric iron in the phase to elemental iron. The aluminium content of C_4AF was bound in the form of C_3A, whereas the excess CaO formed free lime intergrowing with the newly formed elemental iron. Estimations based on chemical composition, molar masses and densities result in a CaO/Fe-volume ratio of 0.85, which roughly coincide with the area ratio of free lime and

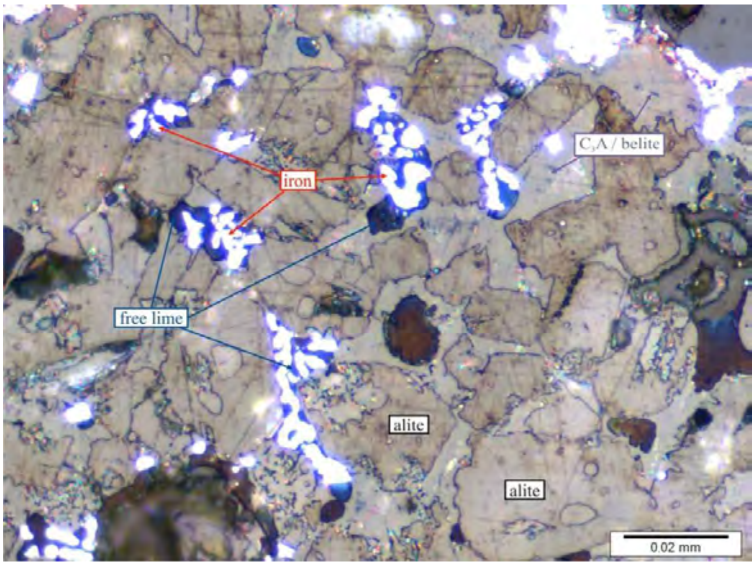

Figure 3: Reflected light micrograph of clinker; symplectites of free lime and elemental iron together with alite crystals in a ground mass free of C_4AF.

iron particles in the symplectitic structures (Figure 3).

The concerned clinker granules must have been exposed to the reducing conditions after passing the sintering zone, since relatively large C_4AF crystals seem to have been the precursor for the free lime-iron symplectites. However, the temperatures must have been high enough to allow for the recrystallization of the ground mass.

References

Bhatty, J.I. (1995): "Role of Minor Elements in Cement Manufacture and Use." *PCA Research and Development Bulletin RD109T*. Portland Cement Association (PCA), Skokie, Ill.

Bhatty, J.I. (2006): "Effect of Minor Elements on Clinker and Cement Performance: A Laboratory Analysis." *PCA Research and Development Bulletin RD130*. Portland Cement Association (PCA), Skokie, Ill.

Böhm, M., Pierkes, R. (2009): "Evaluation of Portland cement clinker with optical microscopy - Case Studies." *Proceedings of the 12th Euroseminar on Microscopy Applied to Building Materials*, Dortmund, Germany, September 15 - 19.

Böhm, M. (2011): "Evaluation of Portland cement clinker with optical microscopy - Case Studies II." *Proceedings of the 13th Euroseminar on Microscopy Applied to Building Materials*, Ljubljana, Slovenia, June 14 - 18.

Campbell, D.-H. (1999): "*Microscopical examination and interpretation of Portland cement and clinker.*" 2. Edition. Portland Cement Association (PCA), Skokie, Ill.

Puntke, S, Schneider, M. (2005): "Effects of phosphate on clinker mineralogy and cement properties." *Cement International*. Vol. 6, No. 5, 80-93

VDZ Verein Deutscher Zementwerke (1965): "Mikroskopie des Zementklinkers." *Beton Verlag*, Düsseldorf.