

## EVALUATION OF PORTLAND CEMENT CLINKER WITH OPTICAL MICROSCOPY – CASE STUDIES II

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### Abstract

Clinker microscopy has been a powerful tool for the evaluation of clinker and cement properties for decades. Microstructural investigations yield important information on phase distribution and the conditions of the phase formation. Two case studies on the application of clinker microscopy are presented, showing the influence of the composition and distribution of raw material and fuel ash particles in the granule on the formation of the clinker phases.

In the first case study, an industrial clinker had been produced with a Ca-source containing organic compounds. These compounds had led to reducing conditions in the clinker granules during the clinker burning process. The typical microstructural effects due to reducing burning conditions (local decomposition of alite to belite and free lime) occurred only in the immediate vicinity of free lime clusters formed by coarse grains of this material embedded in the clinker granules.

The clinker samples from the second case study were produced in the laboratory. In the experiments the agglomeration of Al-rich ash particles on the surface of clinker granules and the incorporation of such particles into clinker granules were emulated. The resulting clinker granules were surrounded by a dense layer of belite and contained belite clusters with central pores, respectively. During the clinker burning process, the Al<sub>2</sub>O<sub>3</sub> had reacted with CaO from adjacent domains in the granules to form calcium aluminates and the calcium rich clinker melt. This had reduced locally the amount of CaO available for the formation of alite and had led to the formation of belite accumulations.

**Keywords: Portland cement clinker; microstructure; case study; burning conditions**

### 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. Many of these materials are waste materials, that are not merely disposed of when used for the production of clinker, but contribute materially to the formation of the clinker phases and help to save fossil fuels and natural raw materials.

However, the use of AFR can influence the clinker properties. Many alternative fuels are introduced into the calciner or kiln in grain sizes that are much higher than those of fossil fuels. Additionally the ash content of some alternative fuels like sewage sludge or used tyres is significantly higher than in fossil fuels. Consequently the burning behaviour of alternative fuels and the incorporation of their residual ash particles in the clinker granules can deviate from fossil fuels.

Many effects of regular or alternative fuels and raw materials (AFR) on clinker properties can be observed with clinker microscopy. The results of two microscopic investigations are presented here performed on a clinker sample from a cement plant and on four laboratory clinker samples produced during a research project on the influence of the use of alternative fuels on clinker properties.

### Sample preparation and analysis

The technical clinker described in the first study was sampled by the producer from a rotary kiln. The clinker samples described in the second study were produced in a laboratory kiln in order to investigate the influence of ash particles inhomogeneously distributed in clinker granules on the clinker microstructure. For this purpose artificial raw meal granules with a diameter of 2 to 10 mm were prepared from raw meals with chemically pure constituents (CaCO<sub>3</sub>, SiO<sub>2</sub>, Al(OH)<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, TiO<sub>2</sub>, CaSO<sub>4</sub>\*2H<sub>2</sub>O) with water in a disk pelletizer. The overall granule composition of the three samples described here were chemically identical. In the mixture No 1 the components were mixed homogeneously. In the mixtures No 2 and 3 only ¾ of the Al(OH)<sub>3</sub> content of the mixture were distributed homogeneously in the granules. In mixture No 2 the remaining ¼ of the Al(OH)<sub>3</sub> was applied with sprayed water as a thin layer on the surface of the granules in order to emulate the introduction of a fuel with an Al<sub>2</sub>O<sub>3</sub>-rich ash into the kiln via the main burner, assuming that ash particles would accumulate on the surface of already formed clinker granules. In mixture No 3 the remaining

¼ of the Al(OH)<sub>3</sub> was granulated with water in a disk pelletizer to form microgranules with diameters of 0.125 to 0.5 mm. These microgranules were added to the homogeneous raw meal before the granulation of the raw meal granules, in order to emulate the introduction of a fuel with an Al<sub>2</sub>O<sub>3</sub>-rich ash into the kiln via the precalciner or the kiln inlet. The Al-rich layer on the raw meal granules (mixture No. 2) and the Al-rich microgranules in the raw meal granules (mixture No. 3) contributed about 1.6 mass % of Al<sub>2</sub>O<sub>3</sub> to the final clinker composition. The raw meal granules were subsequently burned in a laboratory kiln at 1450 °C for 60 min and then immediately taken out of the kiln and let cooled at room temperature.

For the examination of the technical clinker sample with optical microscopy, a representative subsample with a grain size of 2 - 4 mm was obtained by crushing the clinker sample in a jaw crusher and sieving the crushed material. The fraction of the technical clinker and the granules of the laboratory clinker sample were 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 then investigated with an optical microscope under reflected light. The etching procedure enables the distinction of the different clinker phases (alite/C<sub>3</sub>S/Ca<sub>3</sub>SiO<sub>5</sub>; belite/C<sub>2</sub>S/Ca<sub>2</sub>SiO<sub>4</sub>; C<sub>3</sub>A/Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>; brownmillerite/C<sub>4</sub>AF/Ca<sub>4</sub>(Al,Fe)O<sub>5</sub>; free lime/CaO) under the microscope. While the brownmillerite (C<sub>4</sub>AF) 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<sub>3</sub>A 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.

In the first case study an alternative raw material was characterized chemically. The amount of total organic carbon (TOC) was analyzed according to EN 13639, the amount of anorganic bound CO<sub>2</sub> according to EN 196-2. The water content of the material was measured with infrared spectroscopy at 950 °C. The contents of the other oxides listed in Table 1 were analysed with X-ray fluorescence (XRF) on a fused bead. The lower heating value (LHV) of the material was determined acc. to DIN 51900.

## Results - findings of the case studies

### Case study 1: Technical clinker sample

In this case study a typical clinker sample from a cement plant was characterized before changes were performed in the process technology of the plant. An analogous investigation on a clinker sample after these changes allows to observe the resulting differences in the clinker microstructure.

Table 1: Chemical composition of the Ca-rich alternative raw material used in case study 1.

	mass %
TOC	7.3
anorganic CO <sub>2</sub>	36.5
H <sub>2</sub> O	1.1
SiO <sub>2</sub>	1.2
Al <sub>2</sub> O <sub>3</sub>	0.5
TiO <sub>2</sub>	< 0.1
P <sub>2</sub> O <sub>5</sub>	< 0.1
Fe <sub>2</sub> O <sub>3</sub>	0.4
Mn <sub>2</sub> O <sub>3</sub>	< 0.1
MgO	< 0.1
CaO	47.4
sulfate as SO <sub>3</sub>	1.1
K <sub>2</sub> O	< 0.1
Na <sub>2</sub> O	0.6

The clinker sample mainly consisted of the main clinker phases alite, belite, C<sub>3</sub>A and C<sub>4</sub>AF. Additionally it contained a certain amount of clusters of free lime crystals. Free lime clusters are caused by coarse grains of CaO-rich materials (e.g. Campbell, 1999; VDZ, 1965), which lead to a small scale supersaturation of CaO at the grain centre. In the immediate vicinity of many free lime clusters, alite crystals were observed that had partly or completely decomposed to finely intergrown belite and free lime crystals (Figure 1). This phenomenon is an indicator for reduced burning conditions. It is generally caused by the

incorporation of  $\text{Fe}^{2+}$  ions in the crystal structure of alite under reducing conditions in the kiln, which destabilizes the crystal structure of alite and induces its (partial) decomposition (e.g. Sylla, 1981). However, if reducing conditions in the kiln are caused by a general or a local lack of oxygen in the kiln atmosphere or in the clinker bed, respectively, - the latter induced by smouldering fuel particles - the decomposition of alite crystals is not coupled to free lime crystals.

In this case the customer had used a special alternative material with about 47 mass % of CaO, mainly bound as  $\text{CaCO}_3$ , and a certain amount of organic compounds, e.g. 7.3 mass % of total organic carbon (TOC), leading to a LHV of 2042 kJ/kg. The chemical analysis is presented in Table 1. The material was used as a calcium source as well as an alternative fuel and was introduced into the kiln via the kiln inlet. The selective occurrence of signs for reducing conditions near free lime clusters indicates that particles of the described alternative material had caused both phenomenons - the free lime clusters due to their CaO content and the reducing conditions in their direct vicinity due to their content of organic compounds.

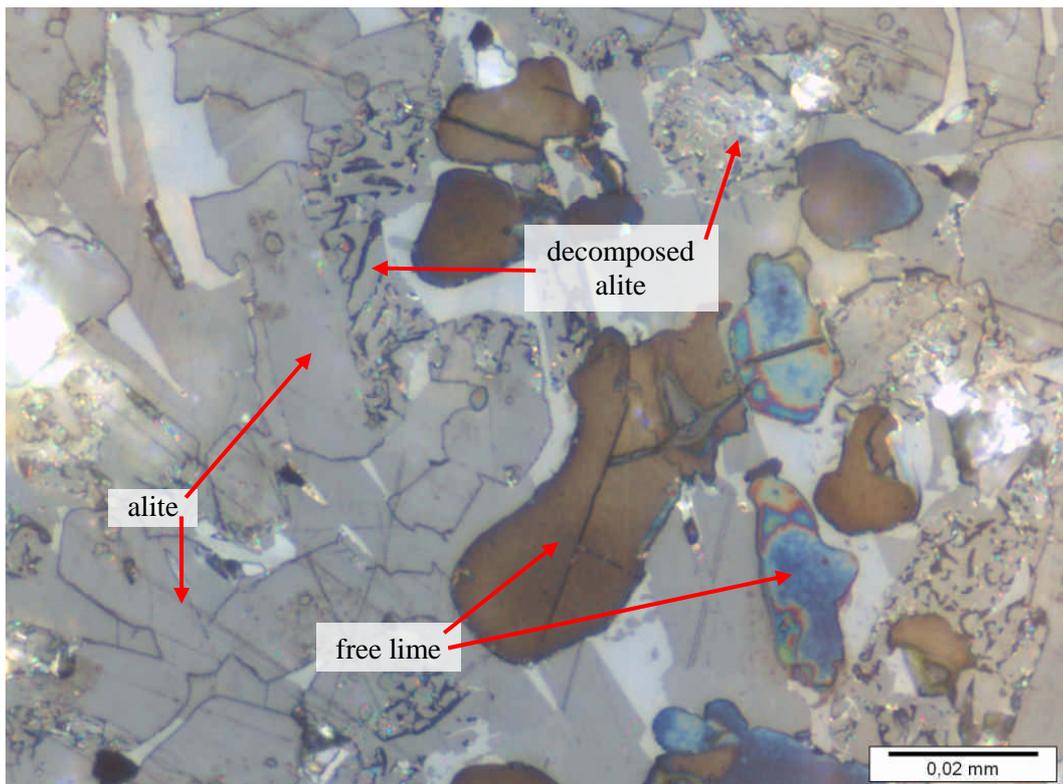


Figure 1: Alite crystals decomposed to belite and free lime in the direct vicinity of free lime crystals forming a cluster

### **Case study 2: Laboratory clinker samples**

In this case study the three laboratory clinker samples produced from the granule mixtures No 1 (homogeneous), No 2 (rim of  $\text{Al}(\text{OH})_3$ ) and No 3 (microgranules of  $\text{Al}(\text{OH})_3$ ) were analysed microscopically. Parallel investigations on the phase composition (XRD) of the three laboratory clinker samples did not show significant differences in the mineralogical composition of the three samples.

The clinker sample produced from the homogeneous raw meal mixture (No 1) had a homogeneous microstructure. The clinker phases were distributed well in the clinker microstructure. The sample contained only a limited amount of small belite clusters.

The clinker granules produced from the raw meal granules with a rim of  $\text{Al}(\text{OH})_3$  (mixture No 2) were surrounded by dense rims of belite crystals with a thickness of about 0.1 to 0.2 mm (Figure 2). These rims contained only very low amounts of ground mass ( $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ ) and no alite crystals (Figure 3). These rims did not occur in clinker granules produced from the homogeneous raw meal granules. In the interior of the granules the distribution of the clinker phases, even the Al-bearing phases ( $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ ) was homogeneous. Even a gradual change of the content of single clinker phases could not be observed, although the raw meal granules had been produced with a strong chemical inhomogeneity.

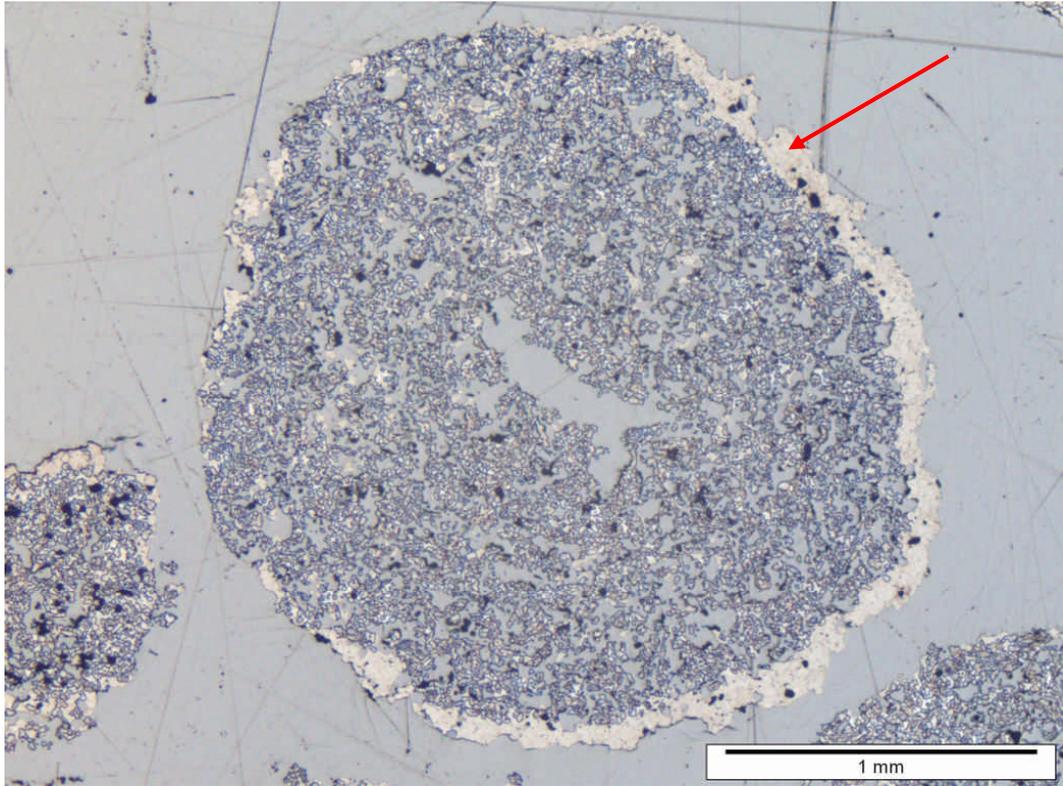


Figure 2: Laboratory clinker granule produced from raw meal mixture No 2 with a dense rim of belite crystals (red arrow)

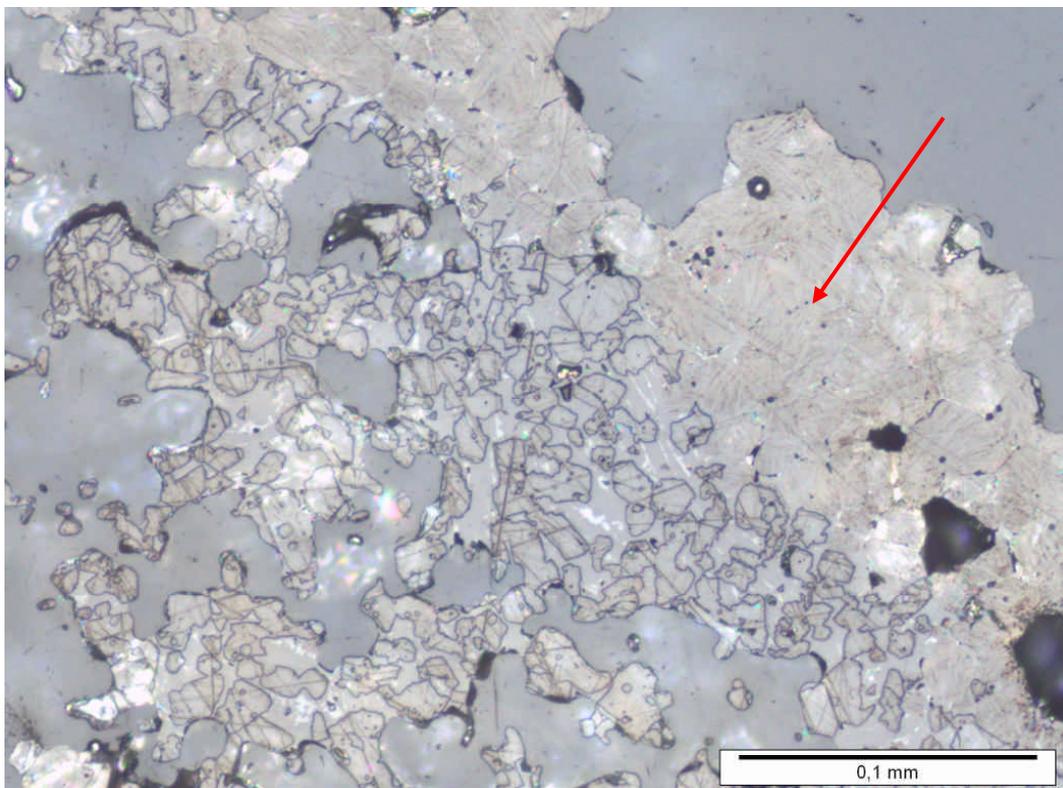


Figure 3: Laboratory clinker granule produced from raw meal mixture No 2 with a dense rim of belite crystals (red arrow); detail from Figure 2

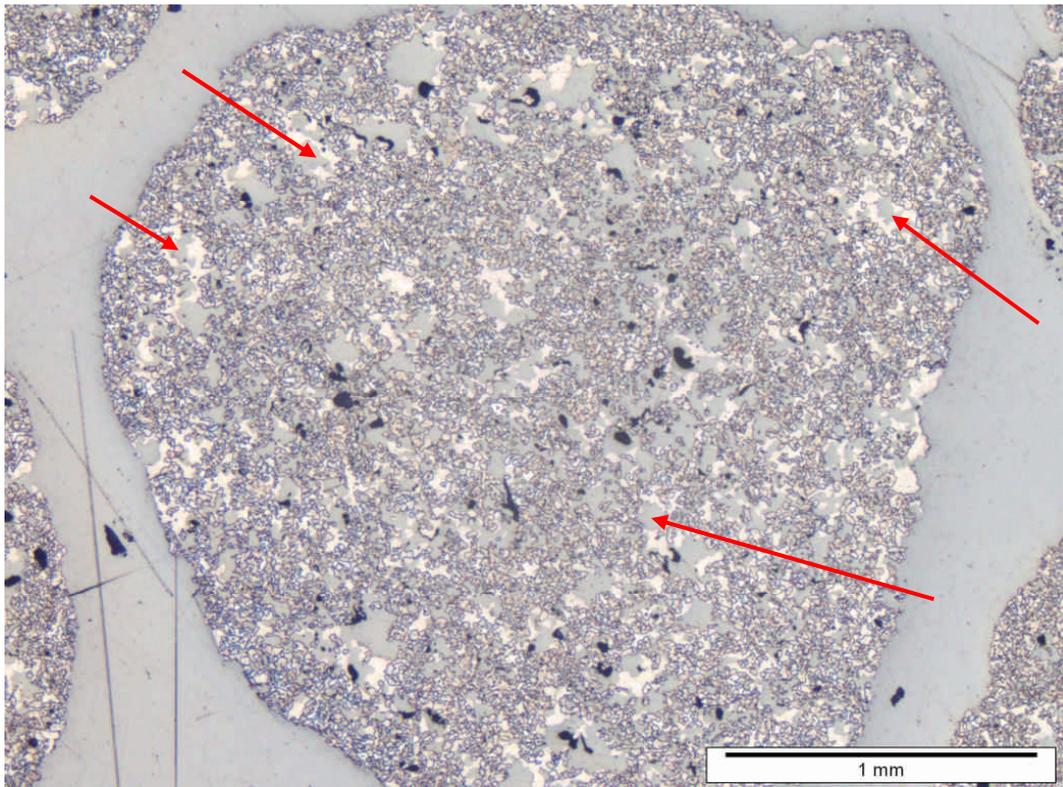


Figure 4: Laboratory clinker granule produced from raw meal mixture No 3 with belite clusters with central pores (red arrows)

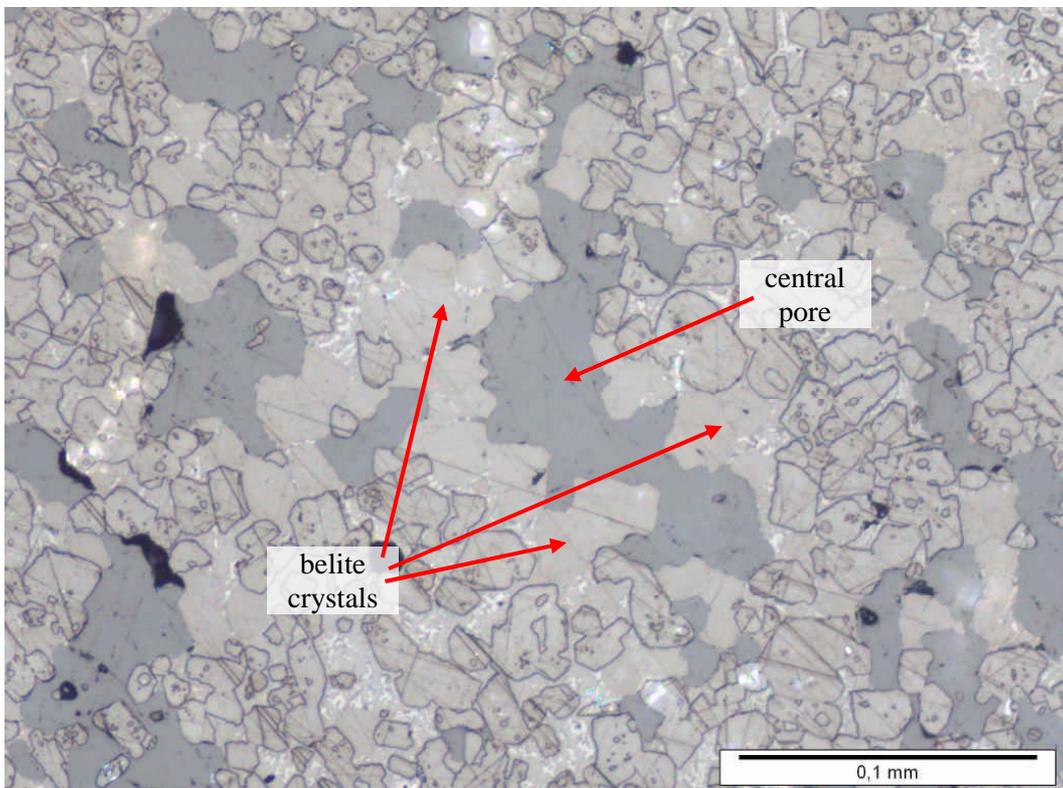


Figure 5: Laboratory clinker granule produced from raw meal mixture No 3 with a circular belite cluster with a central pore; detail from Figure 4

The laboratory clinker produced from the raw meal granules with microgranules of  $\text{Al}(\text{OH})_3$  (mixture No 3) contained a large number of more or less circular belite clusters with central pores and diameters of up to several hundred  $\mu\text{m}$  (Figure 4). The dense layers of belite crystals around the central pores had thicknesses of about 10 to 50  $\mu\text{m}$  (Figure 5). Both laboratory clinker samples produced from mixtures No 1 or 2 did not contain belite clusters with a comparable appearance. Apart from these belite clusters, the distribution of the clinker phases was homogeneous. Local enrichments of Al-bearing clinker phases could not be observed.

The comparison of the microstructures of the three laboratory clinker samples shows that the occurrence of the belite rims and clusters in the clinker samples produced from the raw meal granules of the mixtures No 2 and 3 must have been caused by the inhomogeneous distribution of the  $\text{Al}_2\text{O}_3$ -source in the raw meals. The homogeneous raw meal composition in mixture No 1 did not cause comparable microstructural features. The  $\text{Al}_2\text{O}_3$  itself had been mobile enough during the clinker burning process to distribute itself homogeneously over the clinker granule volume. This can be attributed to the participation of  $\text{Al}_2\text{O}_3$  in the formation of the clinker melt at sintering temperatures. However, the formation of the clinker melt and also of some of the intermediate Al-bearing phases forming during the clinker burning process ( $\text{CA}$ ,  $\text{C}_2\text{A}$ ,  $\text{C}_{12}\text{A}_7$ ) requires  $\text{CaO}$ , which was not present in the Al-rich layers and microgranules. This  $\text{CaO}$  must have been withdrawn from the  $\text{CaO}$ -bearing domains of the granules in the direct vicinity of the  $\text{Al}_2\text{O}_3$ -enrichments (layers and microgranules). The redistribution of the  $\text{Al}_2\text{O}_3$  together with the associated  $\text{CaO}$  over the respective granule volumes left the domains with a reduced  $\text{CaO}$ -content. This local lack of  $\text{CaO}$  inhibits the formation of alite in these domains.

Therefore the formation of the belite rims and clusters in the laboratory clinker samples was not caused by a local enrichment of  $\text{SiO}_2$ , which is usually assumed as the cause for belite cluster formation (e.g. Böhm and Pierkes, 2009; Campbell, 1999; VDZ, 1965), but by an inhomogeneous distribution of  $\text{Al}_2\text{O}_3$  in the raw meal granules. While the initial inhomogeneity was compensated during the clinker burning step, the associated material movement in the clinker granules generated a secondary  $\text{SiO}_2$ -enrichment, resulting in the observed cluster formation. The mineralogical composition of the laboratory clinker samples was not changed by the inhomogeneous distribution of  $\text{Al}_2\text{O}_3$  in the raw meal. The total amounts of belite were comparable in the samples. Only the spacial distribution of belite was affected.

## Summary

The microscopic investigation of technical and laboratory clinker samples and the interpretation of their microstructural features can help to characterize the influence of alternative raw materials and fuels on Portland cement clinker and the clinker burning process.

In the first case study, which was performed on a technical clinker, microscopical investigations revealed minor signs of reducing burning conditions (limited decomposition of alite to belite and free lime). The unusual strict association of these signs with free lime clusters enabled the identification of an AFR as the cause for the reducing burning conditions. This material had been used mainly as a source for  $\text{CaO}$ . Due to a certain amount of organic compounds, it not only functioned as a raw material, but also as an alternative fuel. These compounds had caused reducing conditions in the immediate vicinity of the material particles in the kiln feed. The investigation shows that the use of materials, that are both raw material and fuel for the clinker production process, can lead to a combination of phenomena in the clinker microstructure that used to be typical either for raw materials (here: free lime cluster) or for fuels (here: signs for reducing conditions). In this case, both phenomena could affect the clinker quality when they occur in higher amounts, and a higher fineness of the concerned material could reduce both effects.

In the second case study, which was performed on laboratory clinker samples within a research project, the microscopical investigations showed that the inhomogeneous distribution of  $\text{Al}_2\text{O}_3$  in the raw meal can cause the formation of belite clusters. The formation of belite clusters is usually attributed to local enrichments of  $\text{SiO}_2$ , mostly caused by large grains of quartz or other silicate phases in the raw meal. However, the emulsion of  $\text{Al}_2\text{O}_3$ -rich layers around raw meal granules and of  $\text{Al}_2\text{O}_3$ -rich particles in raw meal granules resulted in belite accumulations in the vicinity of the former  $\text{Al}_2\text{O}_3$ -enrichments. The  $\text{Al}_2\text{O}_3$  must have reacted with  $\text{CaO}$  from the raw meal in its vicinity to form calcium aluminates and the clinker melt. The latter was distributed homogeneously in the clinker granules, leaving areas undersaturated in  $\text{CaO}$  and oversaturated in  $\text{SiO}_2$ , which inhibited the formation of alite and lead to the accumulation of belite. Therefore belite clusters cannot generally be ascribed to coarse  $\text{SiO}_2$ -rich particles, but might also be caused by coarse  $\text{Al}_2\text{O}_3$ -rich particles. However, while the inhomogeneous distribution of  $\text{SiO}_2$  can lead to the formation of higher amounts of free lime in the clinker, the phase composition of the laboratory clinker samples was not affected by the inhomogeneous distribution of  $\text{Al}_2\text{O}_3$ .

These observations enable a more differentiated interpretation of the occurrence of belite clusters. However, the precise mechanism is not yet completely clear, especially the cause for the very low amount of Al-rich ground mass in the belite clusters or rims. The observations have yet to be verified with investigations on technical clinker samples.

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