

# EFFECTS OF ALTERNATIVE FUELS AND RAW MATERIALS ON CLINKER PROPERTIES

Matthias Böhm

VDZ gGmbH, Forschungsinstitut der Zementindustrie, Tannenstraße 2, D-40476 Düsseldorf, Germany,  
Matthias.Boehm@vdz-online.de

## ABSTRACT

Significant amounts of alternative fuels and raw materials (AFR) are used today in the production process of Portland cement clinker. The use of such materials lowers the consumption of natural resources and reduces emissions of carbon dioxide. However, AFR can lead to changes in the clinker mineralogy and microstructure that can be identified with the help of optical microscopy. Three different principles of how the use of AFR can affect the Portland cement clinker properties are described.

The incorporation of raw material and fuel ash particles in the clinker granules and their contribution to the clinker phase formation is dependant on the granularity of the particles, their distribution in the kiln feed and their chemical composition. Like natural raw materials and fossil fuels, coarse SiO<sub>2</sub>-rich and CaO-rich grains from AFR lead to the formation of belite and free lime clusters, respectively. Laboratory experiments showed that coarse Al<sub>2</sub>O<sub>3</sub>-rich particles can also lead to the formation of belite clusters.

Due to their combustion properties some alternative fuels and raw materials can locally lead to reducing burning conditions in the clinker bed, which can result in decomposition of alite to belite and free lime.

The introduction of phosphorous into the clinker system can partially inhibit the formation of alite via a stabilisation of belite, causing the formation of mixed clusters of belite crystals enriched in phosphate and free lime crystals.

## INTRODUCTION

The efforts of the cement industry to advance a sustainable production of cement result from the global needs to conserve natural raw material and fossil fuel resources and as well as to reduce CO<sub>2</sub> emissions. Additionally the economic savings potential resulting from different measures are significant.

A very important measure is the use of alternative fuels and raw materials (AFR). The use of these materials for the production of Portland cement clinker has continuously increased over the last decades. While in 1999 about 23 % of the overall thermal energy demand of German clinker kilns was

substituted by alternative fuels [1], this rate has increased to more than 60 % in 2010 [2]. The total amounts of alternative fuels used in the German cement industry increased from about 0.9 Mt in 1999 to about 2.9 Mt in 2010 (Figure 1).

The most important alternative fuels used in the cement industry are used tyres, animal residues, sewage sludges, waste oil and solid refuse-derived materials from industrial and municipal waste streams [4]. Alternative raw materials are mainly used as corrective materials for single components of the kiln feed, e.g. used foundry sand for  $\text{SiO}_2$  or mill scale for  $\text{Fe}_2\text{O}_3$  [4]. In many cases, the division between fuels and raw materials is not as clear as for fossil fuels and natural raw materials, since many AFR have characteristics of both. For example sewage sludges can contain very high amounts of ash and therefore also contribute significantly to the clinker composition. AFR often differ in chemical composition, humidity, grain size, burning behaviour and other characteristics from fossil fuels and natural raw materials. Therefore the use of AFR for the production of Portland cement clinker can change certain clinker properties. If the clinker quality is affected, the assignment of such changes to the respective cause is crucial for appropriate countermeasures. The cement manufacturers are able to adjust such changes immediately by various measures to produce cements with consistent properties.

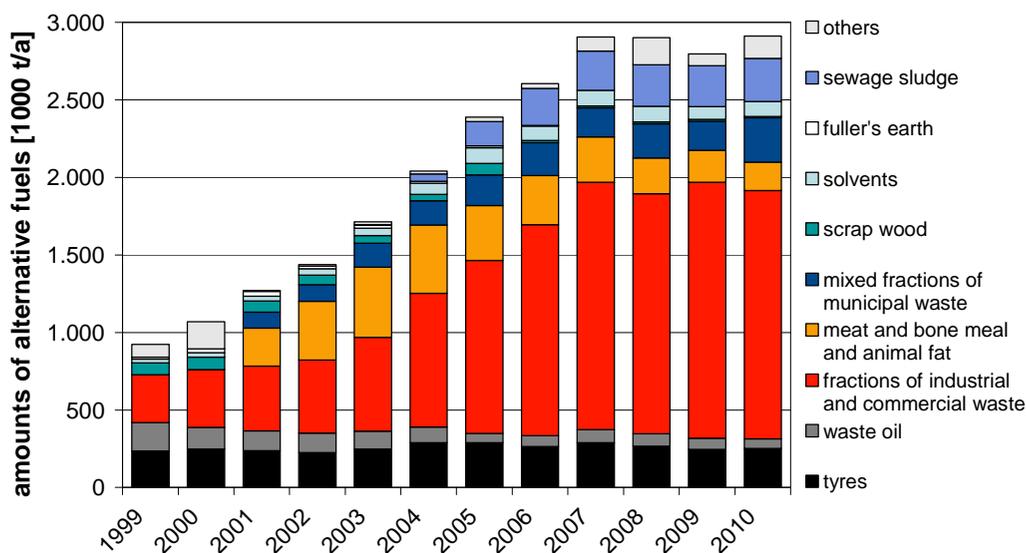


Figure 1: Amounts of alternative fuels used in the German cement industry from 1999 to 2010 [3]

In the following sections, three different principles of how the use of AFR can affect the Portland cement clinker properties are described. In all cases the clinker microstructure is changed and can therefore be identified with clinker microscopy. Several examples observed in clinker samples from cement plants and laboratory experiments are shown.

## SAMPLE PREPARATION

All samples described and shown here were prepared for microscopical analysis according to the following procedure. A representative subsample of each sample was 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  $\mu\text{m}$ . 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/ $\text{C}_3\text{S}/\text{Ca}_3\text{SiO}_5$ ; belite/ $\text{C}_2\text{S}/\text{Ca}_2\text{SiO}_4$ ;  $\text{C}_3\text{A}/\text{Ca}_3\text{Al}_2\text{O}_6$ ; brownmillerite/ $\text{C}_4\text{AF}/\text{Ca}_2(\text{Al,Fe})_2\text{O}_5$ ; free lime/ $\text{CaO}$ ) under the microscope. While the brownmillerite ( $\text{C}_4\text{AF}$ ) 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  $\text{C}_3\text{A}$  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. Free lime appears in a dark grey and/or intense colours of blue or brown with and without etching. The etching procedure can change the appearance.

## CLUSTER FORMATION

Coarse grains in the raw meal can cause local inhomogeneities in the chemical composition of the kiln feed. Due to the local over- and undersaturations of the main clinker components ( $\text{CaO}$ ,  $\text{SiO}_2$ ), this results in the formation of clusters of free lime for large  $\text{CaO}$ -rich grains and in the formation of clusters of belite for large  $\text{SiO}_2$ -rich grains [5, 6]. In both cases, the potential of the system for the formation of alite is not fully exploited. In extreme cases this can affect the cement strength due to a decrease in the alite content and the soundness of the cement due to an increase in the free lime content. Principally the problem of cluster formation can be counteracted with a more intense processing of the raw material in the raw mill, although this can only be applied as long as a higher fineness is economically viable.

Not only natural raw materials, but also AFR are a source for coarse grains in the kiln feed and therefore a possible cause for cluster formation. Ash rich alternative fuels can introduce coarse ash grains into the kiln. Fine grained alternative raw materials are sometimes fed into the kiln without passing the raw mill with the other raw materials so that possible coarse grains are not comminuted. In two case studies the formation of belite and free lime clusters due to the use of alternative raw materials could be verified. Figure 2 shows large belite clusters with central pores. A large number of these clusters had been caused by coarse  $\text{SiO}_2$ -rich grains of unground waste foundry sand that had been used in a kiln trial for the production of the clinker. The number of large belite clusters was significantly smaller in a clinker produced with the same waste foundry sand that had been ground beforehand [7]. Figure 3 shows a free lime cluster, the formation of which could be specifically ascribed to a  $\text{CaO}$ -rich alternative raw material [8]. This alternative material contained organic compounds and caused local reducing burning conditions in the vicinity of its grains (compare section “Local reducing burning conditions”).

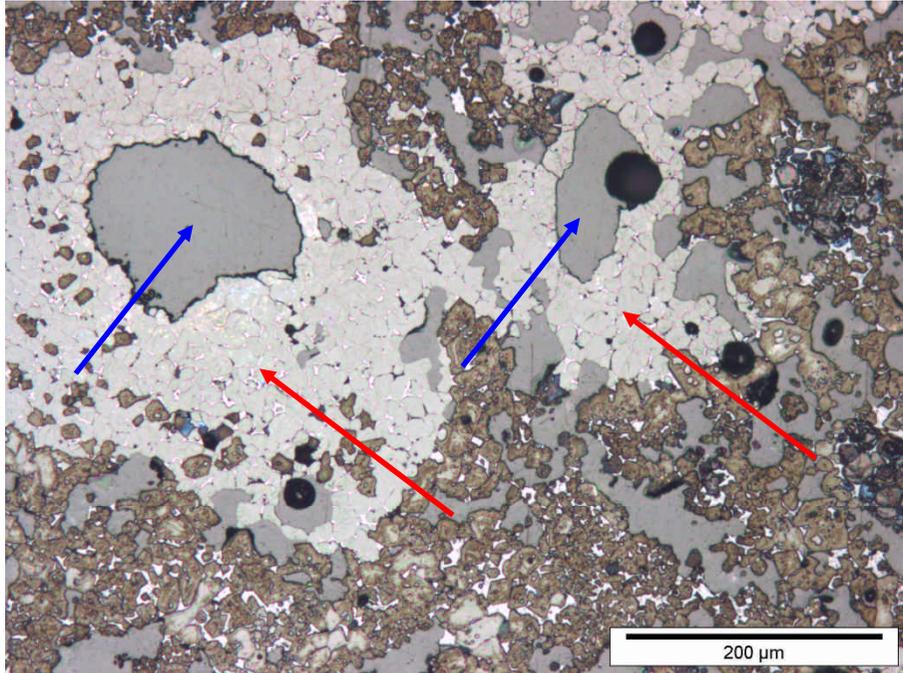


Figure 2: Belite clusters (red arrows) with central pores (blue arrows) due to  $\text{SiO}_2$ -rich alternative raw material (picture from [7])

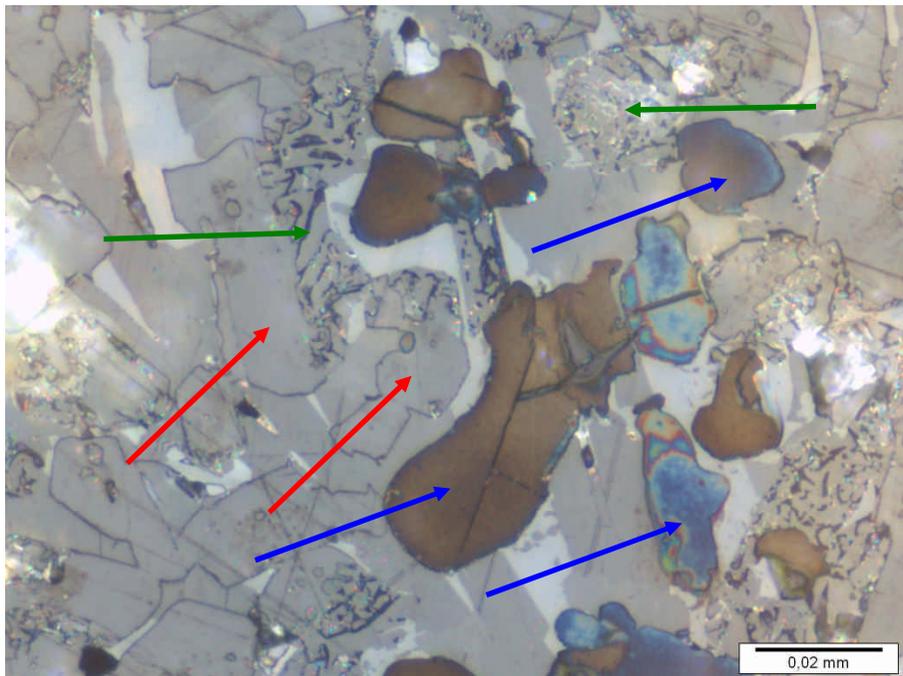


Figure 3: Free lime crystals (blue arrows) forming a cluster due to  $\text{CaO}$ -rich alternative raw material; alite crystals (red arrows) partly or fully decomposed to finely intergrown belite and free lime (green arrows) due to local reducing conditions caused by organic compounds in the  $\text{CaO}$ -source (picture from [8])

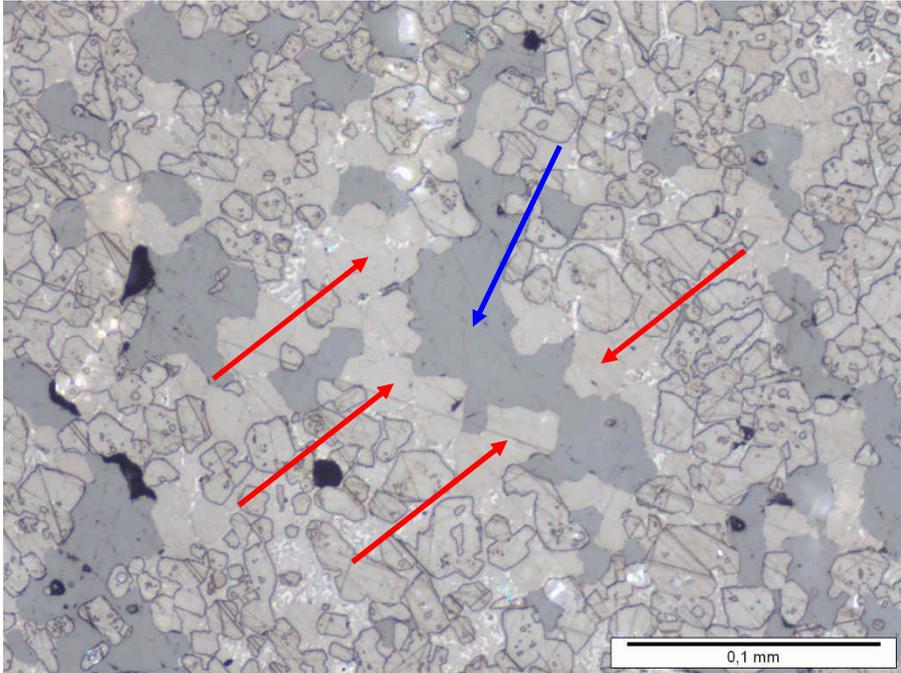


Figure 4: Belite crystals (red arrows) forming a small cluster with a central pore (blue arrow) due to an  $\text{Al}_2\text{O}_3$ -rich particle with approx. the same diameter (laboratory clinker, picture from [8])

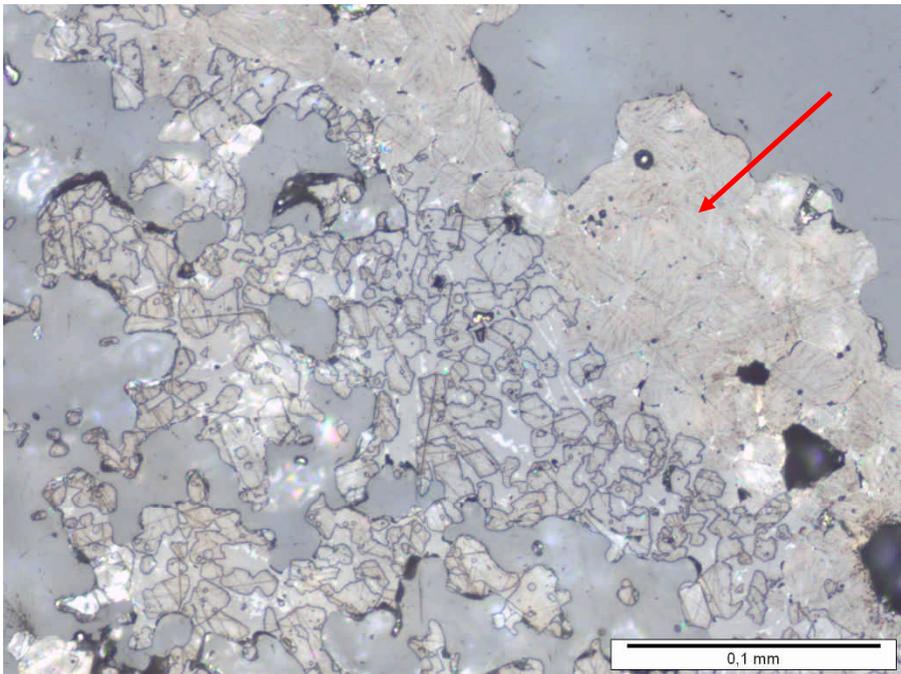


Figure 5: Dense layer of belite crystals (red arrow) forming a rim around a clinker granule, caused by an  $\text{Al}_2\text{O}_3$ -rich layer around the raw meal granule (laboratory clinker; picture from [8])

Unlike natural materials typically used for the production of cement (limestone, marl, clay etc.), AFR can introduce coarse particles rich in Al or  $\text{Al}_2\text{O}_3$  into the kiln. In a research project it was observed in laboratory clinker samples that  $\text{Al}_2\text{O}_3$ -rich particles can cause the formation of belite clusters with central pores (Figure 4) [8]. The formation of the clinker melt and also of some of the intermediate Al-bearing phases forming during the clinker burning process ( $\text{C}_2\text{A}$ ,  $\text{C}_3\text{A}$ ,  $\text{C}_4\text{AF}$ ) requires CaO. This is probably withdrawn from the CaO-bearing domains in the direct vicinity of  $\text{Al}_2\text{O}_3$ -enrichments. The clinker melt itself is mobile during the clinker burning process and is redistributed over the clinker granule volume. This redistribution of the melt containing  $\text{Al}_2\text{O}_3$  and the associated CaO leaves domains with a reduced CaO-content, leading to the formation of belite clusters. The same mechanism can cause dense rims of belite around granules (Figure 5), when the granules are covered with an  $\text{Al}_2\text{O}_3$ -rich layer during sintering. The investigations showed that the clinker mineralogy of the laboratory clinker samples was not changed by the inhomogeneous distribution of  $\text{Al}_2\text{O}_3$  in the raw meal compared to homogeneous samples. Only the spatial distribution of belite was affected [8]. Therefore significant effects on cement properties are not to be expected.

### LOCAL REDUCING BURNING CONDITIONS

The burnout behaviour of alternative fuels can differ significantly from that of fossil fuels. Therefore new burner technologies have been developed over the last decades for an optimal flame control [9]. However, under unfavourable conditions fuel particles that are not completely burned out can fall onto the clinker bed and be buried due to the rotation of the kiln. When the particles keep smouldering under the exclusion of air, they locally cause reducing conditions in their vicinity [7]. But not only alternative fuels can locally cause reducing burning conditions, but also alternative raw materials with organic compounds [8].

The impacts of reducing burning conditions on Portland cement clinker properties are known [e.g. 10]. The most significant microstructural effect is the decomposition of alite to belite and free lime. This decomposition can be restricted to small volumes along crystallographic preferred orientations (Figure 6) or it can affect complete grains of alite (Figure 3). The decomposition is caused by the incorporation of  $\text{Fe}^{2+}$  ions in the crystal structure of alite under reducing conditions, which destabilizes the crystal structure of alite and induces its (partial) decomposition [10]. Under strongly reducing conditions, iron can be reduced to or kept as metallic iron [7, 10]. Figure 7 shows drop-shaped particles of metallic iron in the microstructure of an affected clinker and very small particles of metallic iron as inclusions in alite crystals. The lack of  $\text{C}_4\text{AF}$  in this domain shows that  $\text{Fe}^{3+}$  was not available for the formation of this phase. The groundmass consisted only of  $\text{C}_3\text{A}$ .

The changes of Portland cement clinker properties due to reducing conditions can affect the cement strength due to the decreasing alite content and the setting behaviour of the cement due to the increasing  $\text{C}_3\text{A}$  content.

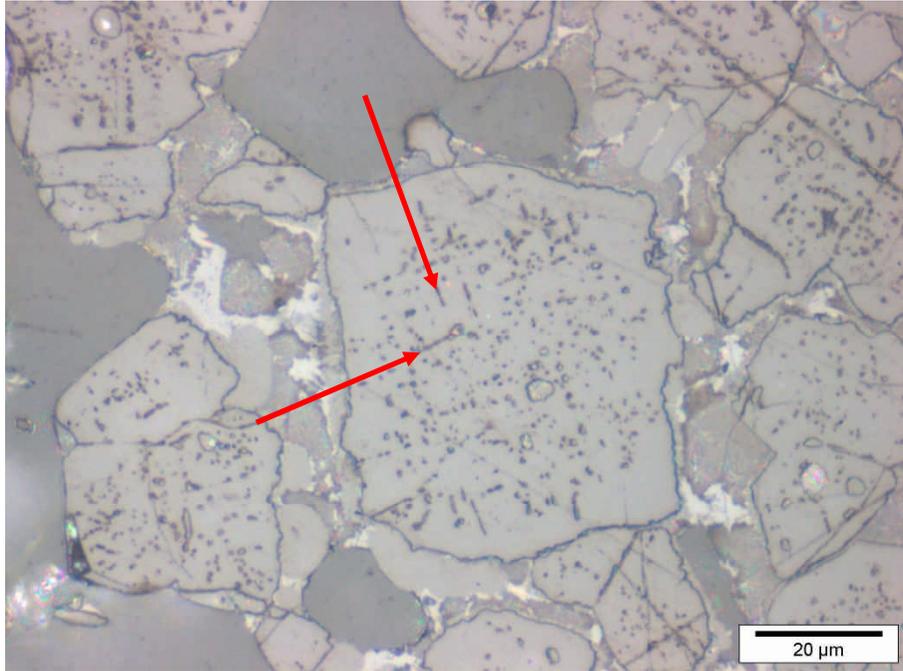


Figure 6: Alite crystals, partly decomposed to belite and free lime along crystallographic preferred orientations (red arrows) due to local reducing conditions (picture from [7])

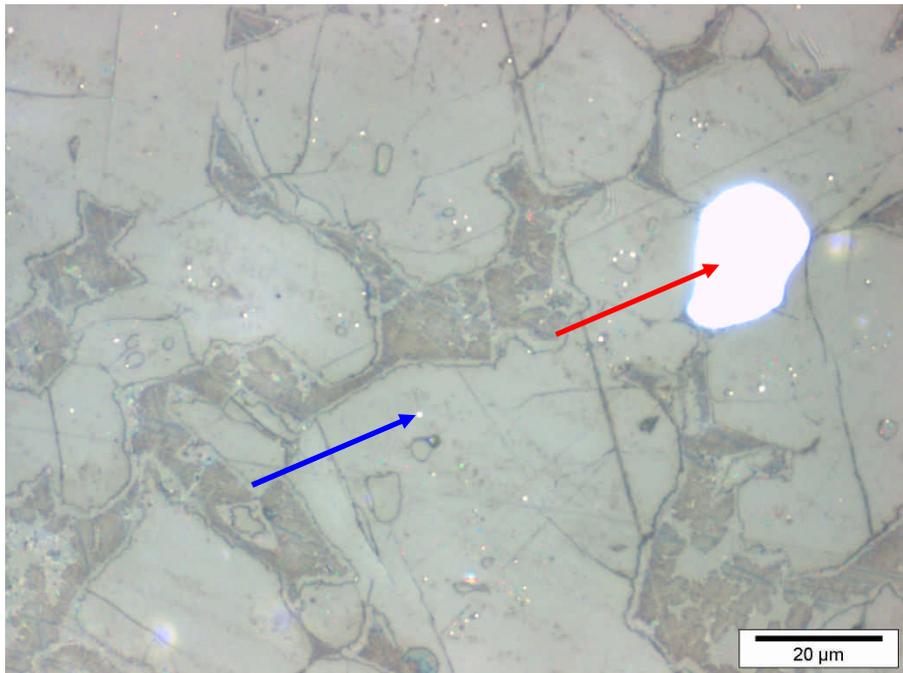


Figure 7: Metallic iron (white) caused by reducing burning conditions forming a 20 μm large droplet (red arrow) and small inclusions ( $< 1 \mu\text{m}$ , blue arrow) in alite crystals (picture from [7])

## INTRODUCTION OF ATYPICAL OXIDES

AFR can introduce different elements in amounts into the kiln, which are atypical for the clinker burning process.  $P_2O_5$  stands out among the non-volatile main element oxides, since it is contained in significant amounts in animal residues and sewage sludges, two important alternative fuels. When  $P_2O_5$  is present in the clinker system, belite enriched in phosphate can form. This is actually a solid solution of belite ( $C_2S$ ) and  $3CaO \cdot P_2O_5$  ( $C_3P$ ). This phase does not react with  $CaO$  to alite at usual sintering temperatures [11]. Under the optical microscope, the solid solution cannot be distinguished from phosphate free belite.

Clinkers produced with animal residues or sewage sludges as alternative fuels often contain mixed clusters of belite crystals enriched in phosphate and free lime crystals (Figure 8). The clusters form due to local enrichments of phosphate in the clinker. The free lime remains unreacted in these clusters, because the formation of alite during sintering is inhibited and the free lime is not consumed. Due to additional ion substitution reactions like  $2SiO_2 \leftrightarrow AlPO_4$  [12], more  $SiO_2$  is available for the clinker phase formation, which can further raise the belite content of the clinker, whereas the amount of  $C_3A$  decreases with rising  $P_2O_5$  content. However, significant changes in the clinker mineralogy cannot be observed at  $P_2O_5$  contents typical also for clinkers produced with animal residues or sewage sludges ( $< 0.6$  m.-%) [3].

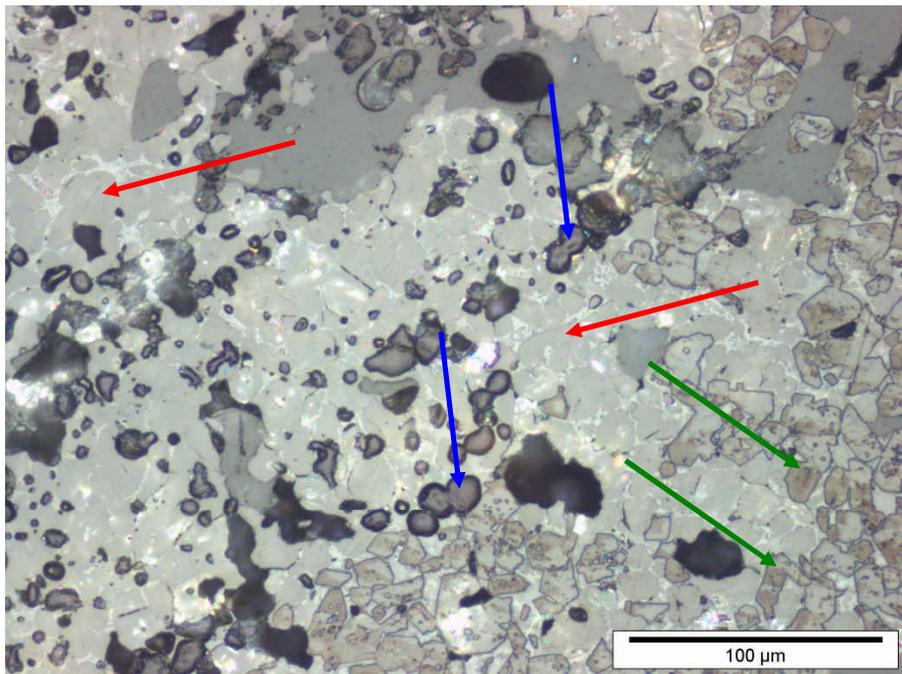


Figure 8: Cluster of belite crystals enriched in phosphate (red arrows) and free lime crystals (blue arrows), surrounded by alite crystals (green arrows; picture from [7])

## CONCLUSIONS

The use of alternative fuels and raw materials in the clinker burning process can lead to changes in the clinker burning process and in the Portland cement clinker properties. The microscopic investigation of technical and laboratory clinker samples and the interpretation of their microstructural features can help to characterize these changes. The analysis of the 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 comparisons of the „before/after” quality of the product help to identify single effects of changes in the materials used in the clinker burning process and to recommend possible corrections of the process.

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 interpreting the findings. Nevertheless, this method enables the cement manufacturer to counteract changes in the clinker properties and to keep a high level of product quality.

## REFERENCES

- [1] VDZ Verein Deutscher Zementwerke e.V. (ed.), “Umweltdaten der deutschen Zementindustrie 1999”, 2000, Düsseldorf
- [2] VDZ Verein Deutscher Zementwerke e.V. (ed.), “Umweltdaten der deutschen Zementindustrie 2010”, 2011, Düsseldorf
- [3] M. Böhm: “Hohe Sekundärbrennstoffraten und hohe Klinkerqualität - kein Widerspruch“ (presentation), Technisch-Wissenschaftliche Zementtagung, 2011, Düsseldorf
- [4] M. Schneider, M. Romer, M. Tschudin, H. Bolio: “Sustainable cement production - present and future”, Cement and Concrete Research 41 (7), 2011, 642-650
- [5] Campbell, D.-H.: “Microscopical examination and interpretation of Portland cement and clinker”, 2nd Edition, 1999, Skokie, Ill. Portland Cement Association (PCA)
- [6] VDZ (Verein Deutscher Zementwerke): „Mikroskopie des Zementklinkers“, 1965, Beton Verlag, Düsseldorf
- [7] M. Böhm, R. Pierkes: “Evaluation of Portland cement clinker with optical microscopy - Case Studies”, Proceedings of the 12<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials, Dortmund, Germany, 15-19 September 2009
- [8] M. Böhm: Evaluation of Portland cement clinker with optical microscopy - Case Studies II”, Proceedings of the 13<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials, Ljubljana, Slovenia, 14-18 June 2011

[9] B. Emberger, H. Hoenig: "Rotary kiln burner technology for alternative fuel co-firing", *Cement International* 9 (5), 2011, 48-60

[10] H.-M. Sylla: "Effect of reductive burning on the properties of cement clinker", *Zement-Kalk-Gips International* 34 (12), 1981, 618-630

[11] S. Puntke, M. Schneider: "Effects of phosphate on clinker mineralogy and cement properties", *Cement International* 6 (5), 2008, 80-93

[12] P. Sulovský, T. Staněk, D. Všíanský: "Hydration of Clinkers with Phosphorus incorporated in the Structure of CA Silicates", *Proceedings of the 12<sup>th</sup> Euroseminar on Microscopy Applied to Building Materials*, Dortmund, Germany, 15-19 September 2009