Influence of Clinker Melt Composition on Reactions at the Surface of Alite Crystals during Cooling

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ABSTRACT

Microstructural features of industrial Portland cement clinker samples are presented to illustrate the influence of the clinker melt chemistry on the reactions taking place on the surfaces of alite crystals during cooling at high temperatures. While clinker melts rich in Al_2O_3 are usually undersaturated with respect to CaO, leading to corrosion of alite crystals and formation of secondary belite, clinker melts rich in Fe_2O_3 are oversaturated with respect to CaO. This leads to a final growth step of alite during cooling, as long as the clinker temperature is still in the stability field of alite (> 1250 °C). In the first case, the microstructural features of the alite surface permits conclusions on the length of the precooling zone in the rotary kiln, which is closely connected to the flame shape. In the latter case, such conclusions cannot be drawn.

KEYWORDS

Alite, alumina ratio, clinker melt, cooling, flame shape

INTRODUCTION

The increased substitution of conventional fuels by alternative fuels in the production process of Portland cement clinker is essential for the decarbonisation of cement and concrete[1]. The use of increased amounts of alternative fuels on the main burner of the rotary kiln often requires modern multi-channel burners, which allow the control of the flame shape. This is necessary because some alternative fuel types like fluff can contain particle types with different burning behaviour due to variations in chemical composition, moisture content, size, specific surface or ignition temperature[2]. In order to optimise the burner settings, information on the flame shape with given burner settings are important.

A widespread method to evaluate the rotary kiln flame characteristics is flame thermography with a pyrometric camera[2]. However, under some circumstances like high dust contents the applicability of the method is restricted[3] or such a system is not available. Therefore other sources of information on the flame shape can be very useful.

For clinkers with alumina ratios (AR = Al_2O_3/Fe_2O_3) > 1.4 the interpretation of the constitution of alite surfaces with clinker microscopy can contribute such information. However, observations on several technical clinker samples presented here show that for clinkers with AR < 1.4 the reactions occurring during cooling lead to different microstructural features that are currently not assignable to certain flame characteristics.

MATERIALS AND METHODS

All observations presented in this paper were made on technical clinker samples. The materials were sampled by the respective producer. The clinker samples were crushed in a jaw crusher and fractions of 2 to 4 mm were retrieved as subsamples from the crushed material by sieving. The subsamples were embedded in epoxy resin under vacuum. After curing, polished sections of the embedded samples were produced. The sections were successively etched with an alcoholic dimethyl ammonium citrate (DAC) solution and with a KOH solution. The etched sections were studied with an optical microscope under reflected light.

The calculation of the alumina ratios (AR) of the samples was based on their chemical compositions, which were analysed with X-ray fluorescence analysis (XRF) on fused beads.

REACTIONS IN CLINKER UPON COOLING

The shape of the main burner flame in a rotary kiln is an important factor controlling the length of the precooling zone, i.e. the last section of the rotary kiln, where the clinker temperature is already decreasing from the temperature in the sintering zone (ca. 1450 °C) due to contact with cooler air entering the kiln from the clinker cooler (secondary air)[4]. A short flame leads to a short precooling zone, while a long flame leads to a long precooling zone.

The clinker usually reaches temperatures of ca. 1200 – 1250 °C in the precooling zone before falling into the clinker cooler[4], which is around or below the lower thermodynamic stability limit of alite[5] and the formation/crystallisation temperature of the clinker melt[6]. Due to the fast cooling of modern technical clinkers, alite is almost always preserved in a metastable state, without signs for decomposition[7]. Microstructural features of the surfaces of alite crystals are therefore only influenced by reactions with the clinker melt, which partly or fully crystallises in the precooling zone. The clinker melt mostly crystallises to C_3A and C_4AF, with minor amounts of periclase and calcium silicates.

Clinker with AR > 1.4

If the clinker melt is rich in Al_2O_3, which is usually the case for clinkers with AR > 1.4, its crystallisation requires more CaO then it contains, i.e. it is undersaturated with respect to CaO. As a result the melt primarily reacts with alite crystals and retrieves CaO from their surfaces[4,7,8]. This effect increases with increasing Al_2O_3 contents[4,8]. The reaction leads to irregular, corroded alite crystal surfaces and, due to the CaO-extraction, to the formation of a rim of secondary belite surrounding the alite crystal. If the precooling zone is short, the system is cooled fast below ~1200 °C and the fine grained rims of secondary belite as well as the corroded alite surfaces are preserved[4,8] (Figure 1A). In a longer precooling zone the clinker is exposed to high temperatures for a longer period of time. This allows coarsening of the secondary belite by collective crystallisation. The belite rings transform into several separate belite crystals around alite. Simultaneously the rough surfaces of alite crystals recrystallise and smoothen (Figure 1B).

Clinker with AR < 1.4

Clinker samples rich in Fe_2O_3 often do not show systematic signs of alite corrosion. On the contrary, microstructural features observed in several technical clinker samples with AR < 1.4 indicate a short final stage of alite growth, most probably occurring during cooling, but at temperatures above the lower thermodynamic stability limit of alite, i.e. in the precooling zone. Figure 2 shows four situations observed in clinker samples with AR < 1.4.

Figure 2A shows alite crystals with uncorroded surfaces and with protrusions (“noses”). These noses seem to expand only the {0001} crystal faces acc. [9], i.e. the basal pinacoids, of the alite crystals and can be explained by lateral growth of these faces. The small size of the “noses” and the growth of the outermost and therefore youngest crystal faces show that the growth step was short and occurred at the very end of the residence time of the material in the alite stability field.

Figure 2B shows alite crystals with signs of zonation, visible due to different etching colours. The outer alite zones are interrupted by belite crystals. The combination of a strongly jagged alite surface with distinct, large belite crystals is very untypical for the reactions described above (alite corrosion, secondary belite formation and recrystallisation). Therefore a different formation mechanism is more plausible. The common starting point of several belite crystals on the same alite zone indicates that the belite crystals grew on a former alite surface. The irregular shape of the belite crystals indicate that the crystals were partly converted into alite, probably while they were overgrown by the outer and therefore younger alite zones, which formed in a final stage of growth.

Figure 2C shows a cluster of belite crystals many of which have small crystals (“crusts”) of alite on their surfaces. Since belite crystals recrystallise and grow in the sintering zone of the kiln, the formation of these “crusts” can be assigned to the kiln section following the sintering zone, i.e. the precooling zone.

Figure 2D shows a cluster of belite crystals. The cluster has a circular center mostly consisting of C_4AF with interspersed lath shaped alite crystals. This phenomenon has been described for Fe_2O_3-rich clinker before and was interpreted as alite crystallised directly from the melt phase during cooling[8]. It shows that the melt contained all constituents for alite formation, including a high amount of CaO. Very similar alite crystals formed on the surface of belite crystals, probably at least partly converting belite into alite. Like the example shown in Figure 2C, the formation of alite on the surface of belite crystals indicates that this reaction occurred at the very end of the clinker’s residence time at high temperatures.

The final short growth step of alite in the precooling zone, as illustrated by the four situations in Figure 2, can be explained by an oversaturation of the Fe_2O_3-rich clinker melt with respect to CaO. When the melt starts to crystallise, the surplus CaO, which is not needed for the crystallisation of C_4AF and C_3A, reacts with belite to form alite. The situation in Figure 2D shows that the CaO can even directly form alite during cooling, together with SiO_2 dissolved in the clinker melt.

CONCLUSIONS

It can be concluded from the observations shown above that the constitution of alite surfaces can presently only serve as a direct indicator for the length of the precooling zone and an indirect indicator for the flame shape, if the alumina ratio (AR) of the corresponding clinker is above 1.4. Otherwise alite crystals are not corroded, but instead grow in the precooling zone. However, it should be kept in mind that, due to local inhomogeneities in the distribution of Al_2O_3 and Fe_2O_3 or other influences, features of alite corrosion and of alite growth can occur in the same clinker sample.

It remains unclear, which of the shown manifestations of alite growth occurs under which circumstances. Additionally it is unclear, if or how different lengths of the precooling zone influence the microstructural features of the final growth step of alite in clinkers with an AR below 1.4. Further systematic observations of Fe_2O_3-rich clinkers should provide this information.

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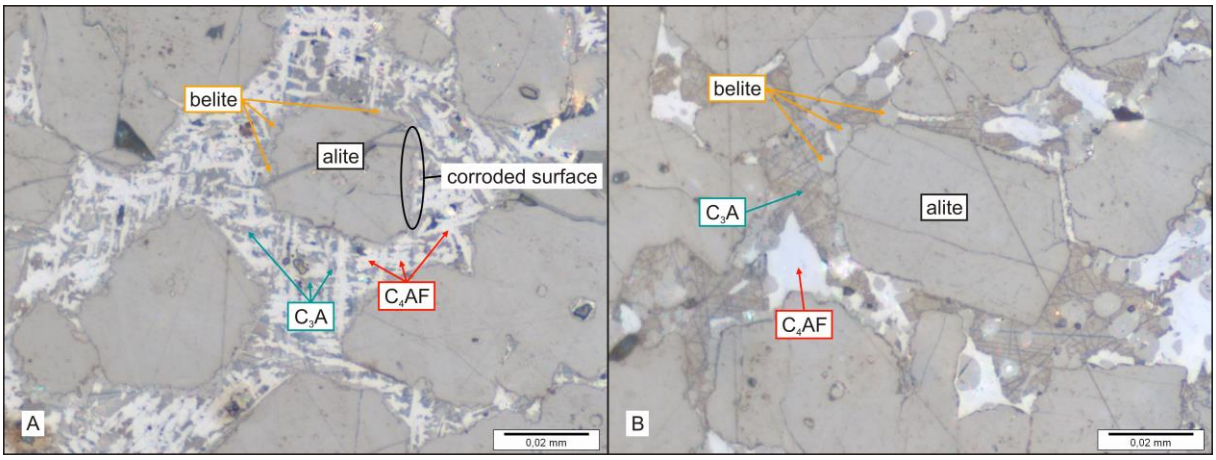

Figure 1: A) alite crystals with corroded surfaces surrounded by thin rims of secondary belite, fine to intermediately fine crystals of C_3A and C_4AF; B) alite crystals with partly corroded, partly smooth surface surrounded by single crystals of secondary belite, coarse crystals of C_3A and C_4AF; both figures taken from [7]

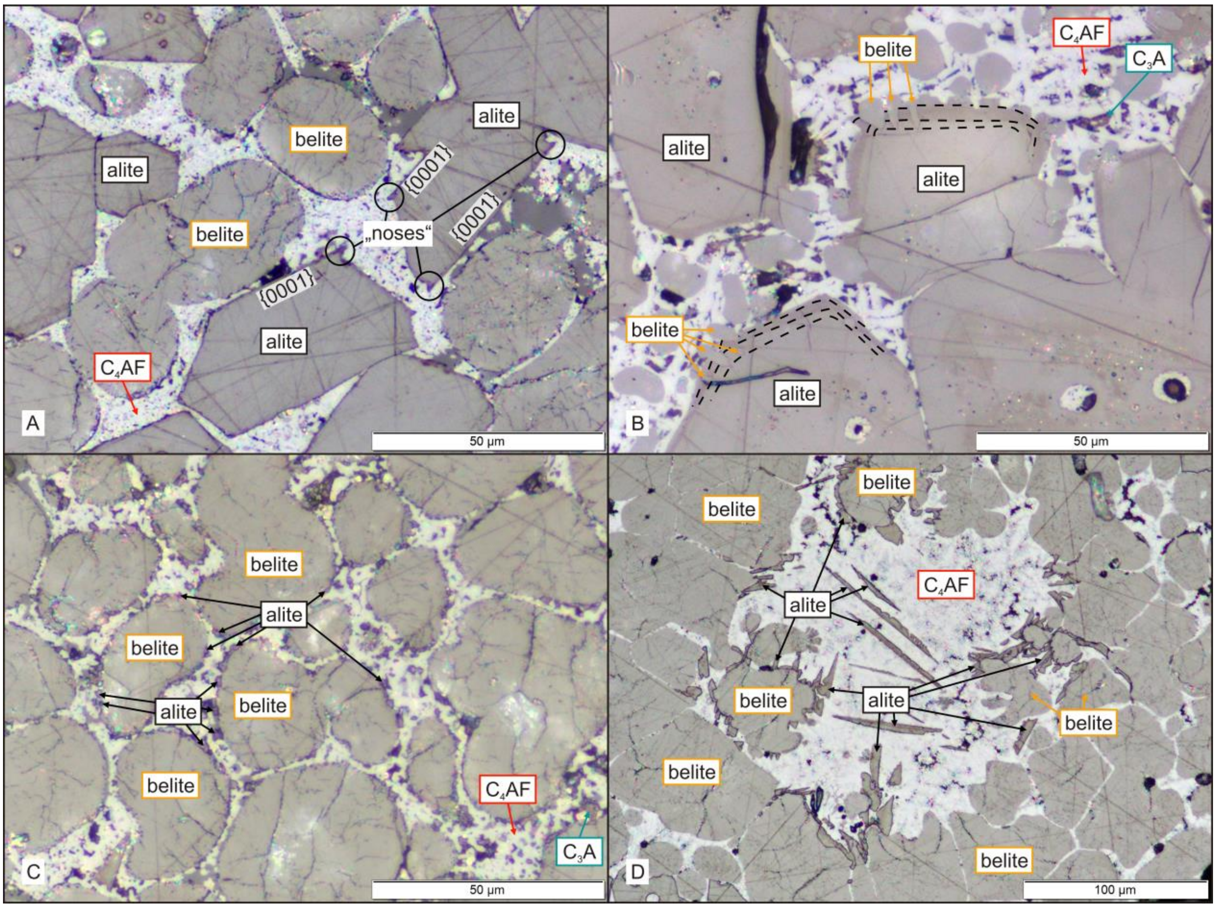

Figure 2: A) alite crystals with uncorroded surfaces, partly with “noses” due to lateral growth of {0001} crystal faces, fine crystals of C_4AF; B) zoned alite crystals with uncorroded surfaces overgrowing belite crystals, dashed lines mark visible zone boundaries, intermediately fine crystals of C_4AF and C_3A; C) “crusts” of small alite crystals on the surfaces of belite crystals, fine to intermediately fine crystals of C_4AF and C_3A; D) cluster of belite crystals, circular center mostly consisting of C_4AF and lath shaped alite crystals formed on the surface of belite crystals or crystallised directly from the melt phase