

ALITE DECOMPOSITION VS. ALITE CORROSION

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Introduction

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. The terminology for the description of microstructures often carries implications about the understanding of the responsible processes. Therefore an unambiguous terminology is necessary to avoid misinterpretations.

The term “alite decomposition” is mostly used to describe the (partial) disintegration of alite crystals, generally resulting in the phases from which alite forms during the clinker burning process, belite and free lime. This is a deleterious reaction that is relatively unusual and affects the clinker quality. The cause should therefore be identified in order to change the process and prevent alite decomposition.

However, sometimes the term it is used to describe a situation that is very common in Portland cement clinker, in which the surfaces of alite crystals disintegrate during cooling, setting free CaO into the melt and resulting in a rim of belite around alite. This reaction is usually not deleterious. To avoid confusion this phenomenon should be called “alite corrosion”.

Causes for alite decomposition

Basically the decomposition of alite can occur when the phase leaves the field of its thermodynamic stability. Pure C₃S crystals are metastable at temperatures below about 1250 °C, while impurities typical for technical Portland cement clinker lowers the stability limit for alite to about 1200 °C [1]. However, the decomposition reaction is strongly controlled by kinetics. C₃S or alite only start to decompose below the stability temperature when it is held at temperatures below the stability limit for long periods (isothermal annealing, e.g. [2], [3], [4], [5]) or cooled with very low cooling rates at temperatures below the stability limit (e.g. [6], [7], [8]). However, in modern technical clinkers low cooling rates enabling residence times at high temperatures (≥ 800 °C) but below the stability limit of alite, comparable to the conditions applied in the cited studies, rarely or never occur. Consequently, in numerous studies performed by the authors of this paper on technical clinker from plants with different preheater, kiln and cooler systems as well as different (alternative) raw materials and fuels, no alite decomposition has been observed that could be ascribed to low cooling rates alone.

When decomposition of alite to belite and free lime occurs in technical clinker, it can in some cases be attributed to the incorporation of oxides like BaO [9], which are unusual for the system and probably shift the alite stability field to higher temperatures [1]. This leads to a longer residence time of the crystals at high temperatures but below the alite stability field, resulting in alite decomposition (Fig. 1a).

The most important cause for alite decomposition in technical clinkers, however, is the incorporation of ferrous iron into the crystal lattice, decreasing its thermodynamic stability [10]. The occurrence of ferrous iron in the clinker burning process is a typical indicator for (mostly local) reducing burning conditions in the clinker bed. Besides belite and free lime (Fig. 1b) sometimes C₄AF occurs as a product of alite decomposition due to reducing burning conditions [10], showing that iron plays an important role in the reaction. The phenomenon of alite decomposition due to reducing burning conditions is relatively rare in modern clinkers, but its correct identification is crucial to allow countermeasures in the process control, since it can strongly affect the cement quality [11].

Causes for alite corrosion

While the decomposition of alite into belite and free lime is rare, alite crystals in technical clinkers are often surrounded by fine to very fine belite crystals [12]. This belite results from the breakdown of alite crystals at their surface. The crystallisation of the clinker melt during the cooling period requires more CaO than is dissolved in the melt. Therefore the clinker melt reacts with the surface of alite crystals during cooling and crystallisation of C₃A and C₄AF, retrieving CaO and leaving a rim of belite (secondary belite) around the remaining alite crystals. The extent of the reaction of the clinker melt with alite is a function of its Al₂O₃ content ([12], [13]). Therefore alite corrosion is stronger in clinkers with higher alumina ratios

(Fig. 1c, 1d, 1f) compared to clinkers with lower alumina ratios (Fig. 1e). The microstructural features resulting from the alite corrosion are controlled by the cooling rate. Fast cooling preserves fine grained rims of secondary belite and rough alite surfaces (Fig. 1c, 1f). Slow cooling leads to coarsening of the secondary belite by collective crystallization, thereby breaking up the belite rim around alite (Fig. 1d). Simultaneously the rough alite crystals recrystallize and smoothen (Fig. 1d).

Since the clinker melt is undersaturated with respect to CaO, it also corrodes free lime crystals during crystallization. Usually this is hard to observe, since it does not lead to secondary phases. Only when early during the cooling period C_3A forms very long lath shaped crystals, which are typical for its alkali rich orthorhombic modification, sometimes signs for the free lime corrosion can be observed (Fig. 1f). Where these long crystals form a more or less perpendicular contact with the surface of free lime crystals at the beginning of melt crystallization, this spot of the free lime surface is protected from further corrosion. On either side the remaining clinker melt reacts with the free lime crystal, extracting CaO. Comparable features occur where the same crystals have a perpendicular contact to alite crystals (in Fig. 1f).

The occurrence of secondary belite around alite resulting from the reaction with the clinker melt is sometimes mistaken as a sign for alite decomposition due to slow cooling. However, the absence of free lime in addition to secondary belite identifies this microstructural feature as the result of alite corrosion and distinguishes it from alite decomposition.

Conclusions

With optical clinker microscopy on polished sections, the superficial alite breakdown due to corrosion by the clinker melt during cooling can be clearly differentiated from the decomposition of alite to belite and free lime. Alite corrosion does only lead to the formation of secondary belite, but not to free lime, because the CaO is consumed by the crystallizing clinker melt.

Apart from the cooling rate, alite decomposition is mainly caused by intrinsic factors, while during alite corrosion, the breakdown of alite is additionally caused by an extrinsic factor. The clinker melt acts as an external “trigger”.

To prevent misinterpretation of microstructural features of Portland cement clinker, it is proposed to use the terms “alite corrosion” and “alite decomposition” like they were used in this paper.

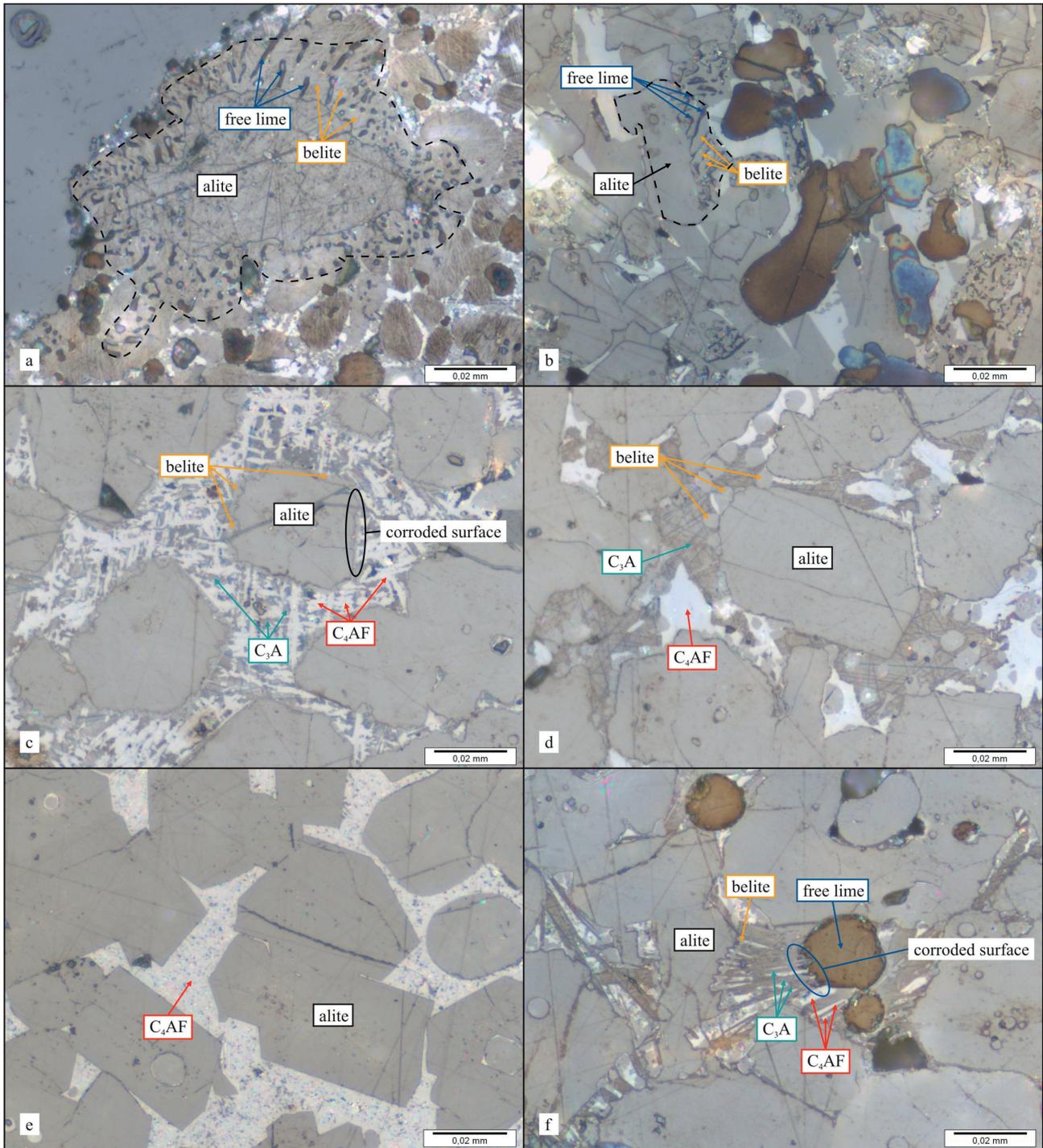


Fig. 1: a) alite crystal partly decomposed to belite and free lime due to high BaO content, dashed line marks former alite surface, photo taken from [9]; b) alite crystal partly decomposed to belite and free lime due to locally reducing burning conditions, dashed line marks former alite surface, photo taken from [14]; c) alite crystals with corroded surface surrounded by thin rim of secondary belite, fine to intermediately fine crystals of C_3A and C_4AF ; d) alite crystals with partly corroded, partly smooth surface surrounded by single crystals of secondary belite, coarse crystals of C_3A and C_4AF ; e) alite crystals with smooth surface, no secondary belite, fine crystals of C_4AF , nearly no C_3A ; f) alite crystals with corroded surface surrounded by thin rim of secondary belite, free lime crystal with corroded surface, intermediately fine crystals of C_3A (lath shaped, orthorhombic modification) and C_4AF

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