

Influences of the oxyfuel cooling medium on mineralogy and microstructure of Portland cement clinker

Matthias Böhm, VDZ gGmbH, Tannenstraße 2, 40476 Duesseldorf, Germany, matthias.boehm@vdz-online.de

Marco Lindemann Lino, VDZ gGmbH, Tannenstraße 2, 40476 Duesseldorf, Germany, marco.lindemann-lino@vdz-online.de

INTRODUCTION

CEMCAP was a project funded by Horizon 2020 addressing CO₂ capture from cement production [1]. Within the framework of this project, VDZ, IKN and HeidelbergCement (HC) have successfully managed to cool clinker under oxyfuel operation conditions in an industrial environment. The oxyfuel clinker cooler prototype was assembled and tested in a HC plant in Hannover [2]. The overall aim of the experimental work was the testing of an oxyfuel clinker cooler in an industrial environment in order to assess its cooling performance as well as the potential impacts of CO₂-rich cooling gas on clinker quality. Despite several experimental challenges, CO₂ concentration levels of the cooling medium higher than 70 vol% have been achieved repeatedly. Moisture content of the recirculated cooling gas was much higher than expected (highest measured value: 13 vol%). This unexpected high moisture content was attributed to the experiment conditions and the lack of a condenser in the prototype setup.

Clinker samples from the cement plant main cooler and from the oxyfuel clinker cooler prototype operated with air and under oxyfuel conditions were taken for further analysis.

EFFECTS ON CLINKER CHEMISTRY, MINERALOGY AND MICROSTRUCTURE

Quantitative X-ray diffraction (QXRD) revealed the presence of up to 1.6 mass% of calcite in some clinker samples from the clinker cooler prototype. Infrared spectroscopy (IR) at 950 °C for CO₂ and H₂O analysis of the same samples showed the presence of up to 0.81 mass% CO₂, confirming the QXRD results.

However, not all samples cooled with a CO₂ rich cooling medium showed significant amounts of calcite or CO₂. One of these oxyfuel samples did not contain more than traces of calcite and only up to 0.12 mass% of CO₂. The same was observed in all clinker samples from the cement plant main cooler and from the oxyfuel clinker cooler prototype operated with air.

The water content of all samples was found to be between 0.11 and 0.28 mass% of H₂O. Portlandite was not observed in any of the clinker samples.

In all clinker samples containing increased amounts of CO₂ and calcite – and only in those samples – unusual layers of up to ~ 2 μm thickness around alite crystals were observed in reflected light microscopy (Figures 1 and 2). A correlation between abundance and thickness of these layers and the amounts of calcite and CO₂ in the respective sample was observed.

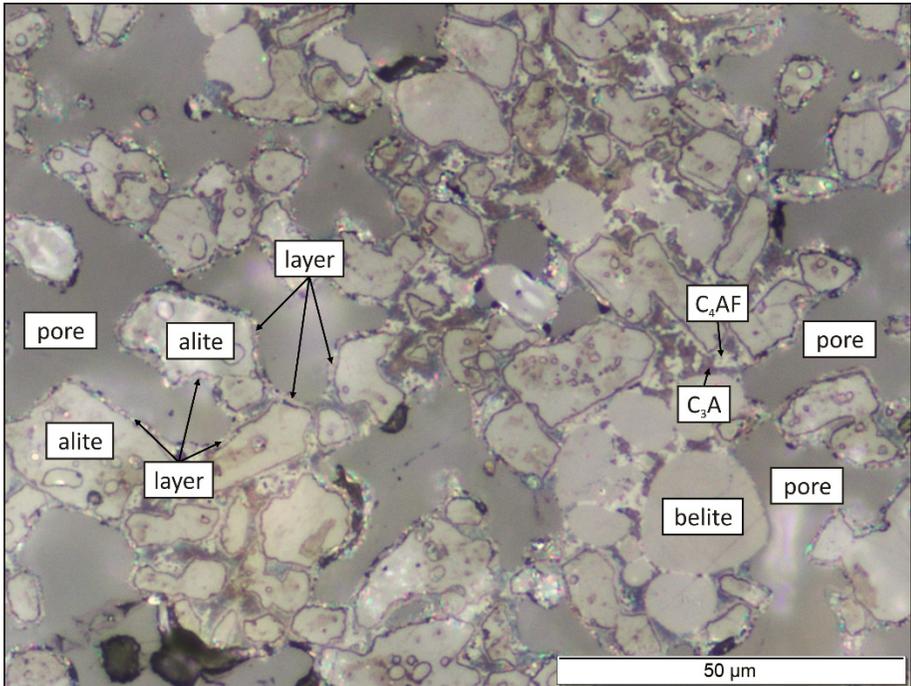


Figure 1: Layer around alite crystals in contact with pores, layer not visible on alite in contact with other solid phases or on other solid phases in contact with pores.

These layers only occurred in alite crystals that were in contact with pores in the clinker, not where it had contact with solid phases (crystals of belite, C₃A, C₄AF, free lime or other alite crystals). The layers did also not occur where other clinker phases (belite, C₃A, C₄AF, free lime) had contact with pores (Figure 1).

Due to the fineness of its constituents, the phase content of the layer could not be unequivocally identified with optical (Figure 2) or scanning electron microscopy (SEM) and electron dispersive X-ray spectroscopy (EDX). However, the EDX analyses did not show the presence of elements other than Ca and Si.

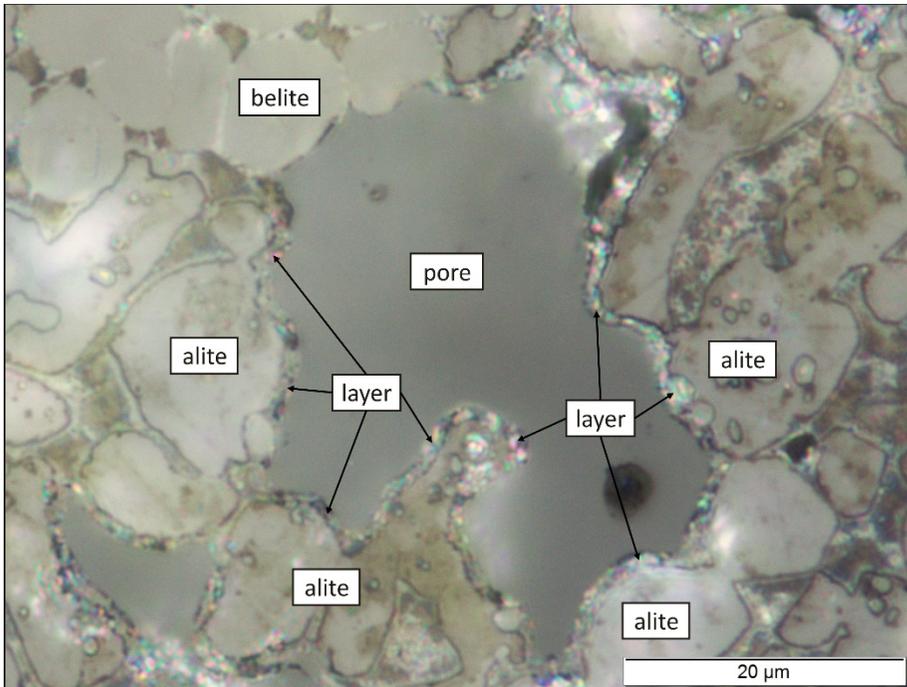


Figure 2: Layer around alite crystals in contact with pores, layer crystallinity too fine for identification.

INTERPRETATION OF THE OBSERVED EFFECTS

Water is known to accelerate alite decomposition at temperatures that are high but already below the stability limit of alite (~ 1250 °C) without being bound in the reaction products [3]. Therefore the high moisture content partly observed in the CO₂-rich cooling medium of the oxyfuel clinker cooler prototype under oxyfuel operation conditions probably caused the decomposition of alite. The decomposition only occurred where alite had contact to the cooling medium, i.e. only around pores, which gave origin to the formation of very fine grained belite and free lime in form of a layer around alite.

Furthermore it can be assumed that subsequently, still during the cooling process, the free lime partly reacted with CO₂ from the cooling medium to form the calcite contents found in the same samples exhibiting the layers around alite. Estimates based on different assumptions suggested that the alite decomposition resulting in the formation of the layer in contact with pores led to a loss of about 2 to 4 mass% of alite in the investigated samples.

The absence of the layer in one sample cooled with CO₂ can be explained by low water contents in the cooling medium. Earlier laboratory investigations on the effects of the

oxyfuel process on clinker characteristics also did not show any comparable effects in clinker burned and cooled with dry CO₂-rich gas [4].

EXPERIMENTAL SUPPORT

In order to support the theory on the formation of the layers around alite a laboratory experiment was performed in which a clinker sample from the plant cooler, which had not shown any layer formation, was exposed to CO₂ and H₂O at high temperatures close to, but still below, the stability limit of alite.

A subsample of the size fraction of 2 to 4 mm of the sample, which had been prepared by crushing and sieving for clinker microscopy, was placed in a platinum crucible. Next to the clinker sample, but not in contact with it, powders of chemically pure Ca(OH)₂ and CaCO₃ were added to the platinum crucible. The platinum crucible was then placed in an aluminium oxide crucible, which was closed with an aluminium oxide lid (Figure 3). The sample container was placed in a static laboratory kiln for the heating experiment under the following conditions: heating up to 600 °C with 1600 °C/h; holding at 600 °C for 30 min; heating up to 900 °C with 1600 °C/h; holding at 900 °C for 30 min; heating up to 1125 °C with 1600 °C/h; holding at 1125 °C for 30 min. Subsequently the crucibles were taken out of the kiln and cooled at ambient conditions. The maximum temperature of 1125 °C was chosen, because the decomposition rate of alite reaches a maximum in the temperature range of 1125 to 1150 °C [3].

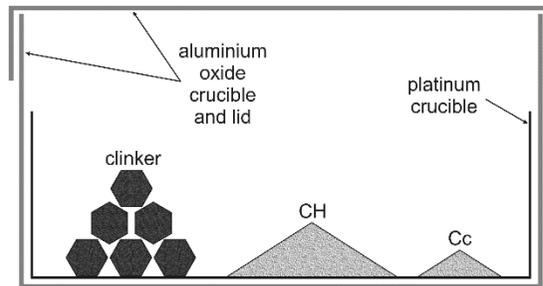


Figure 3: Setup of heating experiment for the reproduction of layers around alite crystals.

Ca(OH)₂ decomposes at ca. 550 °C and releases water vapour. The amount was chosen so that water vapour would completely replace the air in the crucible. CaCO₃ decomposes at > 800 °C and releases CO₂. The amount of CaCO₃ was chosen so that CO₂ would partly replace the water vapour in the crucible. Consequently, the crucibles were filled with a mixture of water vapour and CO₂ at temperatures above ca. 900 °C. This was supposed to simulate the operation conditions, to which clinker was exposed in the cooler prototype. The ratio of CO₂ to water vapor intended in the crucibles was 87 vol% to 13 vol%.

The microscopical analyses on the clinker sample exposed to the described conditions in the heating experiment revealed the occurrence of layers on the surface of alite crystals in contact with pores (Figure 4). In contrast to the samples from the oxyfuel cooler, the crystals forming the layer could sometimes be identified as belite and free lime (Figure 5).

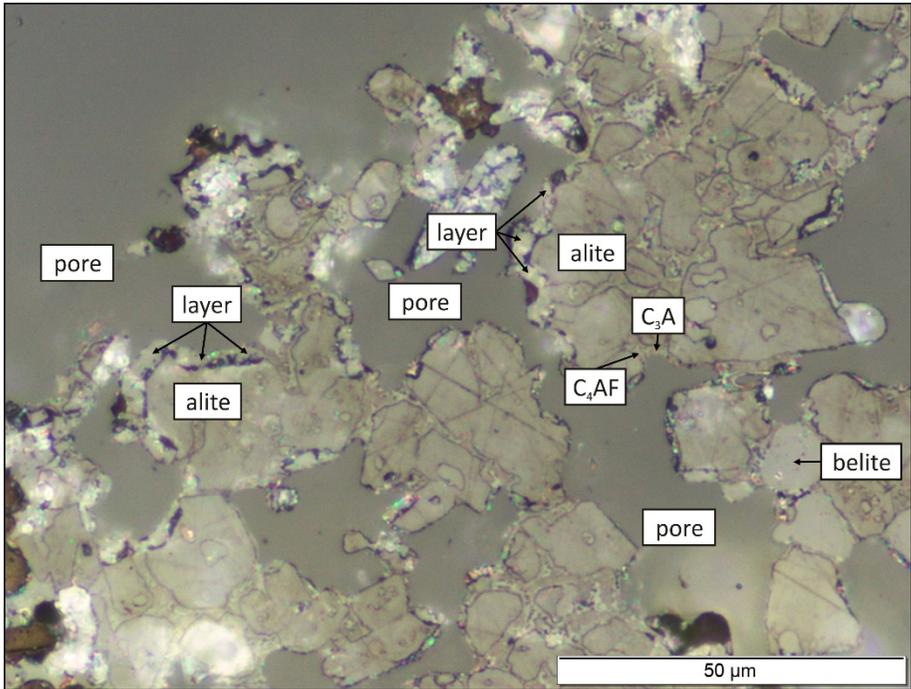


Figure 4: Layer around alite crystals in contact with pores, layer not visible on alite in contact with other solid phases or on other solid phases in contact with pores.

The results showed that the rim around alite could be reproduced with the heating experiment. The observations also showed that the layer on alite crystals in contact with pores mainly consists of belite and free lime, supporting the interpretation that it is the result of a decomposition reaction.

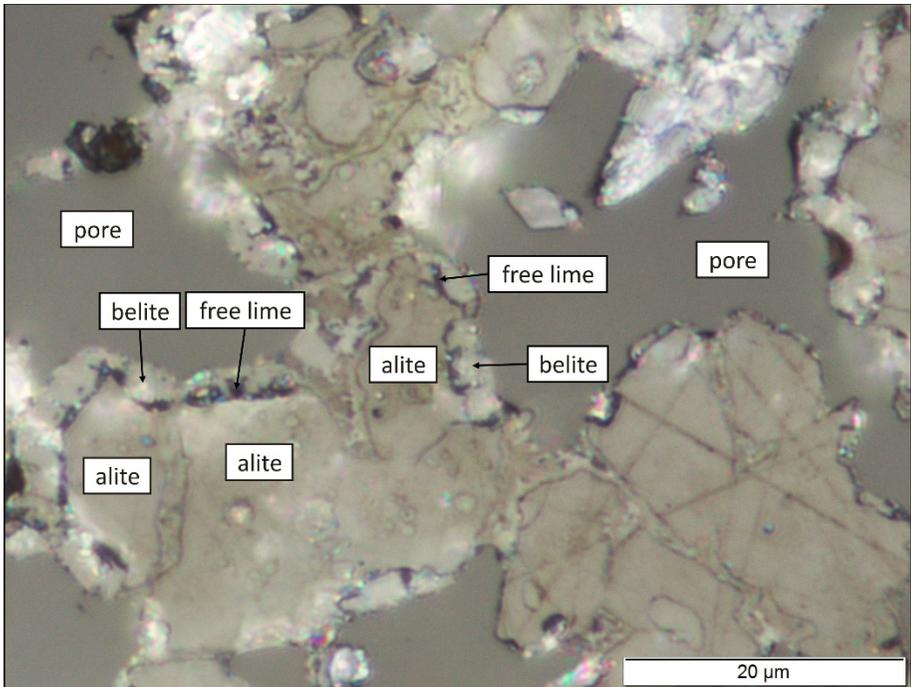


Figure 5: Layer around alite crystals in contact with pores, crystals in the layer partly identifiable as belite or free lime; detail from figure 4.

CONCLUSIONS AND OUTLOOK

The layers on alite surfaces in contact with pores, which had been detected in some of the clinker samples taken from the oxyfuel clinker cooler prototype operated under oxyfuel conditions, mainly consisted of belite and free lime and were caused by a limited extent of alite decomposition. The decomposition reaction had its origin in the contact of alite with a CO₂-rich gas containing water vapour. Contact with such gas mixtures seems to promote alite decomposition at temperatures below its stability limit, i.e. < 1250 °C. Further investigations regarding the correlation between cooling gas composition and alite decomposition rate are recommended.

Additional laboratory testing showed that strength development of cement produced from the clinker samples taken from the cooler prototype was not negatively affected by the observed alite decomposition reaction.

ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 641185.

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