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SUMMARY

VDZ, IKN and HeidelbergCement (HC) successfully tested an innovative oxyfuel clinker cooler prototype in a cement plant in Hanover within the Horizon 2020 CEMCAP project. These tests confirmed that it is possible to successfully cool clinker under oxyfuel operation conditions in an industrial environment. The focus of this paper lies on the assessment of the potential effects of CO_2–rich cooling gas on clinker quality. For this purpose, clinker samples from the plant main cooler and from the oxyfuel pilot cooler were taken for further analysis in VDZ's laboratories. The analysis confirmed that cooling clinker with a CO_2-rich medium in an industrial environment does not have a significant impact on clinker quality. These results confirm the results which had been obtained in a previous laboratory scale experiment [1]. Unusual layers around alite crystals in contact with pores were observed in some clinker samples from the oxyfuel clinker cooler when operated in the oxyfuel mode. Layer formation was correlated with the presence of a cooling medium rich both in CO_2 and moisture. Nevertheless, no negative effects of the layers on cement strength development were observed in additional laboratory testing. The difference of scale between the plant cooler and the oxyfuel cooler had no influence on clinker quality, as no systematic differences in the chemical composition of the samples taken from both coolers when operated in the air mode were found.

ZUSAMMENFASSUNG

Im Rahmen des Forschungsprojekts Horizon 2020 CEMCAP haben VDZ, IKN und HeidelbergCement (HC) erfolgreich einen innovativen Oxyfuel-Klinkerkühlerprototyp in einem Zementwerk in Hannover getestet. Der Versuch hat bestätigt, dass es möglich ist, Klinker unter Oxyfuel-Betriebsbedingungen in industrieller Umgebung erfolgreich zu kühlen. Der Schwerpunkt dieses Artikels liegt auf der Bewertung der potentiellen Auswirkungen des CO_2-reichen Kühlungsmediums auf die Klinkerqualität. Zu diesem Zweck wurden Klinkerproben aus dem Oxyfuel- und dem Werks-Klinkerkühler entnommen, die anschließend im Labor des VDZ analysiert wurden. Die Analysen haben bestätigt, dass sich ein CO_2-reiches Kühlungsmedium nicht wesentlich auf die Klinkerqualität auswirkt. Dies bestätigt die Ergebnisse eines vorherigen Versuchs, der im Labormaßstab durchgeführt wurde. [1]. Bei einigen Klinkerproben aus dem Oxyfuel-Klinkerkühler, die mit CO_2-reichem Gas abgekühlt wurden, traten dort ungewöhnliche Schichten um Alitkristalle auf, wo die Kristalle Kontakt mit Poren hatten. Die Bildung dieser Schichten konnte mit hohen Gehalten an CO_2 und gleichzeitig hohen Feuchtegehalten im Kühlungsmedium in Zusammenhang gebracht werden. Trotzdem wurden in zusätzlichen Laborversuchen keine negativen Auswirkungen der Schichten auf die Zementfestigkeit beobachtet. Die unterschiedliche Skalierung des Oxyfuel-Kühlers im Vergleich zum Werkskühler hatte keinen Einfluss auf die Klinkerqualität, da keine systematischen Unterschiede in der chemischen Zusammensetzung von Klinkerproben aus dem Oxyfuel-Klinkerkühler im Luftbetrieb und aus dem Werkskühler auftraten.

(English text supplied by the authors)

Impacts of the oxyfuel cooling medium on clinker quality

Auswirkungen des Oxyfuel-Kühlungsmediums auf die Klinkerqualität

1 Introduction

The CEMCAP project was a research project conducted by a consortium within the European Union's Horizon 2020 research and innovation programme, which aimed to promote the readiness of technologies for CO_2 capture in cement plants and, thus, bring them closer to deployment. For the capturing of CO_2 in cement plants three key-technologies of the oxyfuel process were tested (clinker cooler, calciner and burner). This work is based on the experiment conducted by VDZ, IKN and HC, whose aim was the testing and operation of the world's first oxyfuel clinker cooler prototype in an industrial environment (Technology Readiness Level 6). The construction and testing of the oxyfuel clinker cooler on a pilot scale were based on previous research conducted by ECRA within its Oxyfuel Project. One of the major concerns identified by ECRA was the potential reaction of CaO contained in the alite and belite clinker phases (C_3S and C_2S respectively) with CO_2 in the cooling medium and a consequent loss of clinker quality. Experiments conducted by ECRA at lab-scale revealed that the impact of a high CO_2-concentration in the cooling medium on the clinker quality and the resulting cement properties were negligible and that the required clinker quality could be met [1]. Given the vital importance of clinker quality on product viability, the conduction of tests with hot clinker in an industrial environment was required to validate the promising lab results. Thus, the test of the oxyfuel clinker cooler prototype had the following main objectives:

- Determine false air in-leakage
- Determine the gas leaking rate to ambient
- Determine the clinker cooling curves and cooling efficiency with CO_2-rich gas
- Determine the influence of cooling gas composition on clinker chemistry

The focus of this paper is exclusively on the potential effects of CO_2-rich cooling gas on clinker quality and cement strength development. In order to simulate clinker cooling under oxyfuel conditions, hot clinker taken from the kiln hood of the plant was routed to the cooler prototype with the help of an innovative extraction system. In addition, CO_2 concentrations over 67 vol. % in the cooling medium were achieved and maintained during the trials (❱ Table 1). Clinker samples from the cement plant main cooler and from the oxyfuel clinker cooler prototype were taken periodically. The experimental challenges and results with respect to the objectives 1 to 3 were presented and discussed before in a paper published in this journal [2]. One relevant result of the measurements during the experiment was a moisture content in the cooling medium well above 1 vol. %. Without any sources of water in the cooling gas recirculation circuit, this result was unexpected. The reason for such high moisture content in the cooling medium as well as the accuracy of the measurements remains unclear and questionable, but some possible explanations were discussed in that paper [2]. The presence of this moisture produced some effects not only on clinker mineralogy but also on the performance of the cooler grate plates.

2 Characterisation of the clinker samples

In total nine clinker samples were taken and subsequently analysed (s. Table 1). Two clinker samples taken from the cooler prototype when it was operated with air (S1_air, S2_air) were homogenized before analysing the resulting mix sample (S3_air). Five clinker samples were taken from the cooler prototype, when it was operated with CO_2-rich gas and two clinker samples were taken from the plant cooler simultaneously with the tests of the cooler prototype. The samples S3_air to S10_air were analysed with regard to their chemical composition, their mineralogical composition and their microstructure.

Table 1: Clinker samples and cooling media

Setting	Short name of the sample	Cooling medium	Cooling equipment
1	S1_air	air	Clinker cooler prototype
2	S2_air	air	Clinker cooler prototype
1-2	S3_air	air	Clinker cooler prototype
3	S4_oxy	CO_2-rich gas (84 vol. % CO_2)	Clinker cooler prototype
4	S5_oxy	CO_2-rich gas (67 vol. % CO_2)	Clinker cooler prototype
5	S6_oxy	CO_2-rich gas (75 vol. % CO_2)	Clinker cooler prototype
6	S7_oxy	CO_2-rich gas (75 vol. % CO_2)	Clinker cooler prototype
7	S8_oxy	CO_2-rich gas (76 vol. % CO_2)	Clinker cooler prototype
3-4	S9_air	air	HC clinker cooler
5-7	S10_air	air	HC clinker cooler
Note: More information on operation conditions can be found in [2]			

The chemical analyses were carried out with X-ray fluorescence (XRF) on fused beads according to EN 196-2 [7] for main oxide composition. The contents of CO_2 and H_2O were measured with infrared spectroscopy (IR) at 950 °C. The mineralogical compositions of the clinker samples were examined with quantitative X-ray diffraction (QXRD). The powder samples were analysed within a diffraction angular range of 5 to 80 degrees (2 degrees Theta, Cu $K\alpha$ radiation). The minor clinker phases were analysed by measuring the X-ray diffraction patterns of the clinker samples after dissolving the silicate phases and the free lime in a methanol/salicylic acid digestion (M/S digestion). The X-ray diffraction patterns were evaluated quantitatively with the Rietveld refinement method. The micro-

Table 2: Chemical composition of two representative clinker samples

Component	ØS3_air	S5_oxy
CO_2	0.12	0.36
H_2O	0.28	0.15
SiO_2	21.89	21.90
Al_2O_3	5.42	5.50
TiO_2	0.35	0.30
P_2O_5	0.17	0.17
Fe_2O_3	1.71	1.68
Mn_2O_3	0.04	0.04
MgO	1.00	1.00
CaO	66.78	67.11
SO_3	0.73	0.60
K_2O	0.78	0.78
Na_2O	0.31	0.33

structure of the clinker samples was evaluated with reflected light microscopy on polished sections. The sections were prepared from subsamples of the 2 to 4 mm fraction of the crushed clinker samples. The 2 to 4 mm fraction samples were embedded in low viscosity epoxy resin under vacuum. After curing, polished sections were produced and etched with alcoholic dimethyl ammonium citrate (DAC) solution as well as 2.5 % KOH solution. The sections were studied with an optical microscope under reflected light. The chemical and mineralogical compositions of all clinker samples, as well as their most important microstructural features, were comparable. The analytical results of two samples showing all important features discussed in this paper are listed in ❱ Table 2 (chemistry) and ❱ Table 3 (mineralogy).

The water content of all samples was found to be between 0.11 and 0.28 mass % of H_2O. Portlandite was not observed in any of the clinker samples. However, four of the five pilot cooler samples taken during operation with CO_2-rich gas (S5_oxy, S6_oxy, S7_oxy and S8_oxy) showed unusually high contents of CO_2 (0.36 to 0.81 mass %). Corresponding amounts of calcite (0.6 to 1.6 mass %) identified with QXRD in the same samples show that the CO_2 is mainly bound in this phase (❱ Fig. 1).

Table 3: Mineralogical composition of two representative clinker samples

Component	ØS3_air	S5_oxy
Alite	64.7	62.6
Belite	17.1	16.6
C_3A	13.7	14.1
C_4AF	2.3	3.1
Free lime	0.7	1.9
Periclase	traces	traces
Quartz	traces	< 0.5
Calcite	traces	0.6
Arcanite	0.6	< 0.5
Aphthitalite	0.6	< 0.5

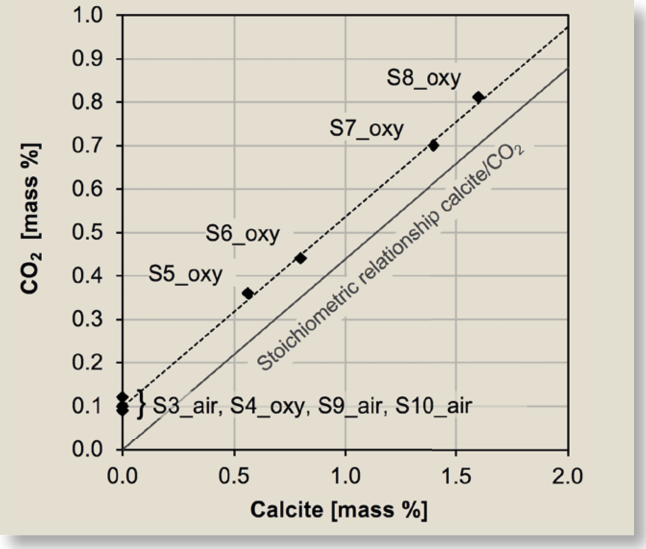

Figure 1: Correlation between calcite and CO_2 content of four clinker samples with unusually high contents of each

The other four samples (S3_air, S4_oxy, S9_air and S10_air) contained only ca. 0.1 mass % (0.09 to 0.12 mass %) of CO_2 and no calcite. Only in those clinker samples containing increased amounts of CO_2 and calcite unusual layers of up to ~ 2 µm thickness around alite crystals were observed in reflected light microscopy (❱ Figs. 2 and 3). Abundance and thickness of these layers were lowest in the sample S5_oxy and highest in the sample S8_oxy, indicating a correlation to the amounts of calcite and CO_2 observed in the respective sample. The observed layers only occurred where alite crystals were in contact with pores in the clinker, not where it had contact with solid phases (crystals of belite, C_3A, C_4AF, free lime or other alite crystals). The layers also did not occur where other clinker phases (belite, C_3A, C_4AF, free lime) had contact with pores (s. Fig. 2). Due to the fineness of its constituents (s. Fig. 3), the phase content of the layer could not be unequivocally identified by light or scanning electron microscopy.

3 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 CO_2-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 the form of a layer around the alite.

Furthermore, it can be assumed that during the cooling process, the free lime partly reacted with CO_2 from the cooling medium to form the calcite contents found in the same samples, which exhibited the layers around the alite. An estimate based on plausible inner surfaces of clinker (0.02 m²/g), an alite content of 65 vol. %, an intermediate thickness of the observed layer of 0.5 µm and the density of alite (3.15 g/cm³) results in up to 2 mass % of decomposed alite in the samples. A further estimate, based on stoichiometric calculations and the assumption that the calcite (up to 1.6 mass %) in the clinker samples was formed from free lime, which itself formed due to alite decomposition, leads to up to 4 mass % of decomposed alite in the samples. Both estimates are in the same order of magnitude.

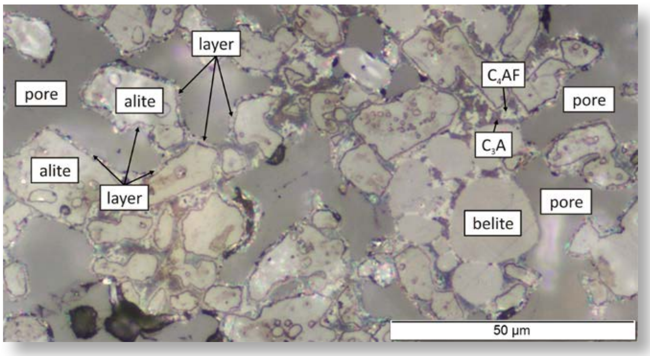

Figure 2: Layer around alite crystals in contact with pores, layer not visible on alite in contact with other solid phases or on other solid phases in contact with pores

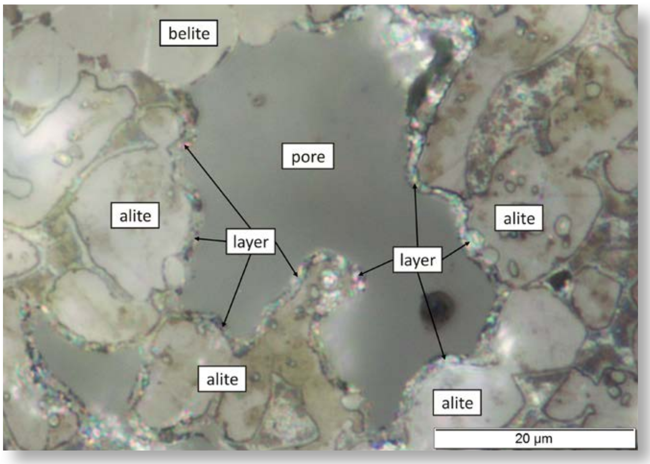

Figure 3: Layer around alite crystals in contact with pores, layer crystallinity too fine for identification

The absence of the layer in one sample cooled with CO_2 can be explained by low water contents in the cooling medium. This assumption is confirmed by earlier laboratory investigations on the effects of the oxyfuel process on clinker characteristics, which did not show any comparable effects in clinker burned and cooled with dry CO_2-rich gas [4].

4 Confirmation by laboratory experiment

In order to support the theory on the formation of the layers around alite a laboratory experiment was performed. A clinker sample from the plant cooler, which had not shown any layer formation, was exposed to CO_2 and H_2O at temperatures of 1 125 °C, which are 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 $CaCO_3$ 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 (❱ Fig. 4).

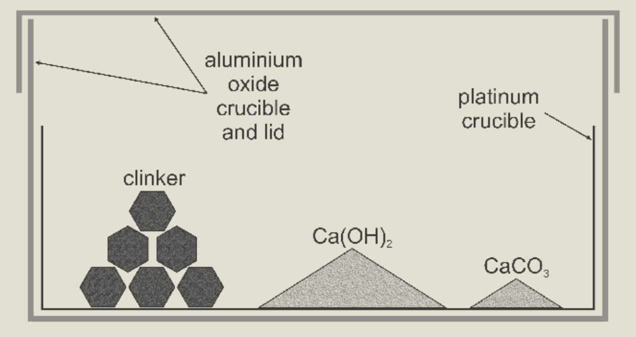

Figure 4: Setup of heating experiment for the reproduction of layers around alite crystals

The sample container was placed in a static laboratory kiln for the heating experiment under the following conditions: heating up to 600 °C with 1 600 °C/h; holding at 600 °C for 30 min; heating up to 900 °C with 1 600 °C/h; holding at 900 °C for 30 min; heating up to 1125 °C with 1 600 °C/h; holding at 1 125 °C for 30 min. Subsequently the crucibles were taken out of the kiln and cooled at ambient conditions. The maximum temperature of 1 125 °C was chosen because the decomposition rate of alite reaches a maximum in the temperature range of 1 125 to 1 150 °C [5]. $Ca(OH)_2$ 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. $CaCO_3$ decomposes at > 800 °C and releases CO_2. The amount of $CaCO_3$ was chosen so that CO_2 would partly replace the water vapour in the crucible. Consequently, the crucibles were filled with a mixture of water vapour and CO_2 at temperatures above approx. 900 °C. This was intended to simulate the operating conditions to which clinker was exposed in the clinker cooler prototype. The desired gas mixing ratio in the crucibles was 87 vol. % CO_2 to 13 vol. % water vapour. The microscopical analyses of 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 (❱ Fig. 5). In contrast to the samples from the oxyfuel clinker cooler prototype, the crystals forming the layer could sometimes be identified as belite and free lime (❱ Fig. 6). The rim around the alite could be reproduced with the heating experiment. The observations support the interpretation that layer formation is the result of alite decomposing to belite and free lime.

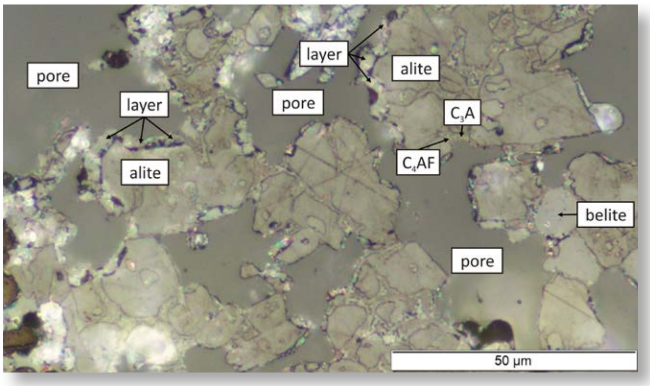

Figure 5: Layer around alite crystals in contact with pores, layer not visible on alite in contact with other solid phases or on other solid phases in contact with pores

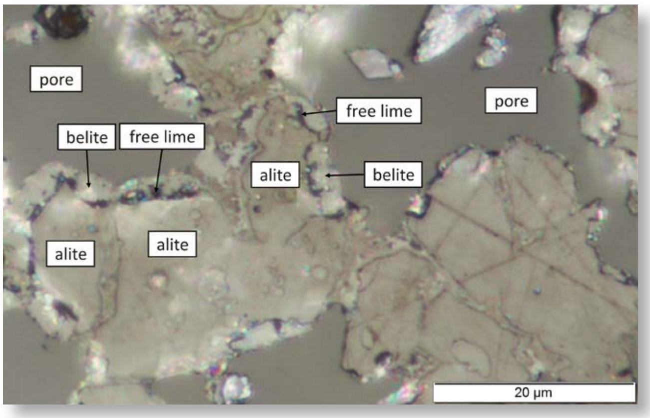

Figure 6: Layer around alite crystals in contact with pores, crystals in the layer partly identifiable as belite or free lime; detail from Fig. 5

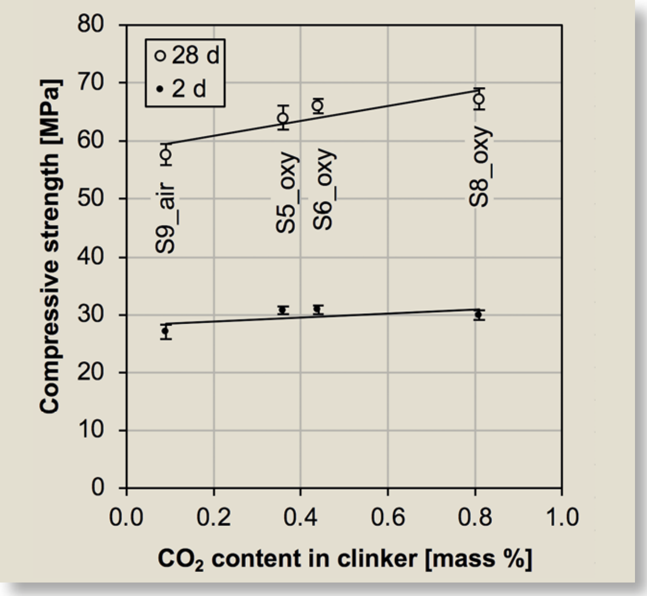

Figure 7: 2 d and 28 d compressive strength (with twofold standard deviation) of the laboratory samples plotted against the CO_2 content of the respective clinker sample

5 Impact on cement strength

In order to investigate if the observed alite decomposition would have any negative effect on the strength development of cements produced with the affected clinker, several clinker samples were used to produce laboratory cement. The 2 d and 28 d compressive strengths of these cements were tested. Four clinker samples were selected for the experiments (S9_air, S5_oxy, S6_oxy, S8_oxy). The samples differed in their calcite and consequently in their CO_2-content, which was interpreted as an indicator of the alite decomposition reaction. One of the selected samples (S9_air) was selected as a reference sample. It did not show any signs of alite decomposition.

The clinker samples were ground to a comparable fineness (3 340 to 3 400 cm^2/g acc. to Blaine). Subsequently, the ground clinker was mixed and intensely homogenised with sulphate carriers (anhydrite and hemihydrate). The total addition of sulphate with sulphate carriers (2.2 mass %) and the respective contents of anhydrite and hemihydrate (1.8 mass % SO_3 from anhydrite, 0.4 mass % SO_3 from hemihydrate) were equal for all laboratory cements. The 2 d and 28 d strength of the laboratory cements were then tested according to EN 1961 [8].

The 2 d and 28 d compressive strengths of the laboratory cements are plotted against the CO_2 content of the cements in ❱ Fig. 7. The samples in which alite decomposition had been observed show no indication of strength loss in cement compared to the reference sample without signs of alite decomposition. We therefore conclude that in the range of alite decomposition observed in the pilot cooler trial, no negative impact of the specific mechanism of alite decomposition on strength development is to be expected. On the contrary, the laboratory cements produced from pilot cooler samples (S5_oxy, S6_oxy, S8_oxy) showed higher 28 d strengths than the reference (S9_air, sample from plant's cooler). The effects on the 2 d strengths are much weaker. This can partly be explained by the different cooling history of the samples. The mineralogical and microstructural analyses of the clinker samples had shown that the samples from the pilot cooler had been precooled in the extraction system and cooled faster in the pilot cooler than the samples from the plant main cooler, probably due to grain size effects. Fast precooling of clinker with high alumina ratios like in this case (approx. 3.2) can positively influence the 28 d strength [6].

6 Conclusions

Cooling clinker with a CO_2-rich medium in an industrial environment does not have a significant impact on clinker quality. 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 amount of alite decomposition (2 to 4 mass %). Nevertheless, no negative impacts on cement strength development were observed due to the limited alite decomposition reaction. In addition, it was confirmed that the decomposition reaction had its origin in the contact of alite with a CO_2-rich gas containing unusually high amounts of water vapour. Contact with such gas mixtures seems to promote alite decomposition at temperatures below its stability limit, i.e. < 1 250 °C. Such an effect will be minimized in a future oxyfuel cement plant with the installation of a condenser upstream from the clinker cooler, as already envisaged by ECRA [2]. Further investigations regarding the correlation between cooling gas composition and alite decomposition rate are recommended.

Acknowledgements

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