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Modelling of clay calcination: Rotary kiln versus flash calciner

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ABSTRACT

The worldwide availability of suitable clays makes calcined clays a very promising pozzolanic supplementary cementitious material (SCM) for further lowering the clinker content in cements. Thus, CO_2 emissions from fuel combustion and decarbonation of limestone during clinker production can partially be saved, but must be assessed against respective CO_2 emissions from the calcination process of the clay.

With regard to the future increase in demand for calcined clays in the context of decarbonization, significantly more rotary kilns and flash calciners will be built or retrofitted for clay calcination. In this study the energy demand and CO_2 emissions of both technologies were simulated for a clay production rate of 500 t/d depending on the clay's mineralogy and moisture. The CO_2 emissions for a calcination at around 800 °C range between 0.1 and 0.3 kg CO_2/kg calcined clay, depending on the type of calcination and the mineralogy and moisture of the clay.

It can however be stated that calcination in a flash calciner appears to be more efficient than calcination in a rotary kiln, both in terms of energy and CO_2 emissions.

KEYWORDS: *calcined clay, cement, rotary kiln, flash calcination, modelling*

1. Introduction

The ecological assessment of common composite cements is possible due to sufficient data on the CO_2 emission of their main components like slag and others. For the calcination of clays of different compositions, these data are lacking so far. They are required for assessing the CO_2-emissions and -savings of the production of clay-containing cements.

For example, Vizcaino et al (2015) indicate a CO_2 saving potential of 30 % for the use of calcined clays in composite cements with 55% clinker compared to an OPC. Hernandez and Scrivener (2015) and Sanchez Beriell et al (2015) derive saving potentials of 15 to 20 % from demonstration projects in Cuba. Scrivener (2014 and 2016) considers savings of up to 300 to 350 kg CO_2/t cement to be achievable. The values correspond approximately to the data given in ECRA (2017), where CO_2 saving potentials are estimated for the use of calcined clays in composite cements with clinker contents of 65 wt.%. Compared to cements commonly used today with an average clinker content of 75 wt.%, the saving potential is about 70 kg CO_2/t cement, and in relation to OPC slightly more than 200 kg CO_2/t cement. More detailed specifications taking into account the clay composition and the production process are mostly not available, but necessary.

2. Experimental work and simulation

The calcination of two different Calcite containing clays (cf. Table 1) in a rotary kiln and in a flash calciner was simulated. In order to be able to compare the results, the same initial parameters (moisture, fuel, phase composition, calcination temperature, etc.) were used in each case. The production rate was assumed to be 500 t/d for both simulated plants.

Table 1: Phase composition of the used clays W1 and W2, wt.%

Clay	Kaolinite	Illite	Chlorite	Calcite	Others (Quartz etc.)
W1	10	40	8	7	35
W2	4	18	4	30	44

Based on the composition of the clays (cf. Table 1), the interlayer water content of the individual clay minerals (Kaolinite: 12 wt.%, Illite: 8 wt.%, Chlorite: 15 wt.%), was calculated. This water content was related to the water content and the theoretical heat of formation of Kaolinite (H_R= 418 kJ/kg Kaolinite), so that all clay minerals were treated as Kaolinite in the simulation. Thus, the theoretical heat input for the dehydroxylation of all clay minerals at the respective temperature could be calculated in a simplified way.

The theoretical heat input for the decomposition of the carbonates was determined from the reaction of $CaCO_3$ to CaO and CO_2 at the respective temperature and the theoretical decomposition enthalpy of Calcite (H_R= 1780 kJ/kg $CaCO_3$). From the heat input for dehydroxylation and decomposition, the total theoretical heat requirement for calcination of the clays could be calculated (cf. Table 2). Via the specific energy content and CO_2 contribution of the fuel (in this case coal with 26300 kJ/kg and 66,90 wt.% C), it is possible to determine the specific CO_2 emissions for the calcination of the respective clay and also for the production of corresponding clay-containing cements with 20 wt.% calcined clay.

Table 2: Theoretical heat input for the calcination of the clays (dehydroxylation of the clay minerals and decomposition of the carbonates) depending on the temperature, kJ/kg product

Clay	Dehydroxylation of clay minerals			Decomposition of carbonates			Total		
	600 °C	800 °C	1000 °C	600 °C	800 °C	1000 °C	600 °C	800 °C	1000 °C
W1	125	151	178	0	15	129	125	166	307
W2	55	66	77	0	65	615	55	131	692

3. Results

The calculated CO_2 emissions caused by the calcination of the two clays consist of combustion-related and raw material-related CO_2. Therefore, the different Calcite contents of the clays have a particularly large influence on the amount of CO_2 emitted as soon as the respective clay is calcined at the temperature level of 800 °C or higher, which leads to the decomposition of the Calcite (cf. Figure 1).

At the temperature level of 600 °C, the CO_2 emissions are only combustion-related because $CaCO_3$ decomposition has not yet started and therefore the emissions correspond to the fuel-related CO_2 emissions. Depending on the calcination technology for a raw clay with 20 wt.% moisture the emissions were between about 0.12 and 0.17 kg CO_2/kg calcined clay. With increasing temperature and carbonate content, the CO_2 emissions increase caused by the decomposition of the Calcite and the higher fuel input. When calcining at 800 °C, the CO_2 emissions ranged between about 0.14 and 0.22 kg CO_2/kg calcined clay, depending on the technology. At 1000 °C, the decomposition of the Calcite is completely finished and the entire material-bound CO_2 is emitted. For clays containing carbonates, a firing temperature of more than 800 °C is therefore not recommended due to higher CO_2 emissions.

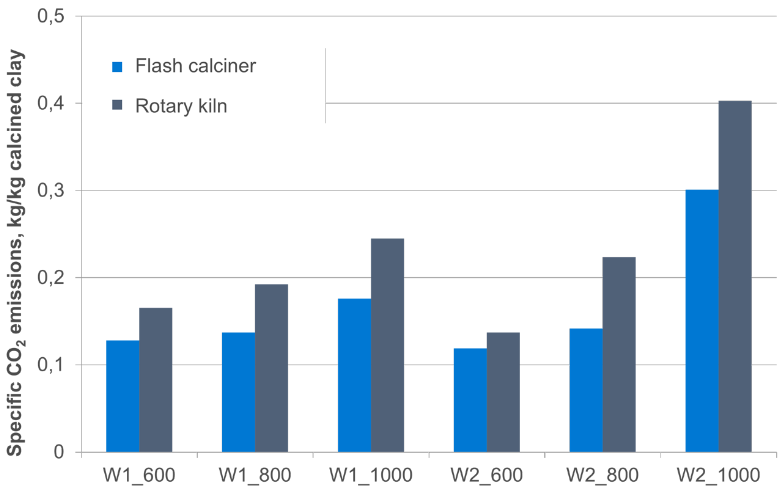

Figure 1: Specific CO_2 emissions of the calcination of clay W1 and W2 at different temperatures (600, 800 and 1000 °C); order of designation: clay_temperature

According to the simulation, the calcination in the flash calciner was more efficient than the calcination in the rotary kiln, both in terms of energy and CO_2 emissions. A fundamental advantage of the flash calciner is the improved energy exchange between gas and material, among other things due to the good mixing of the flows in the cyclone stages compared to the heat transfer through the material bed in the rotary kiln.

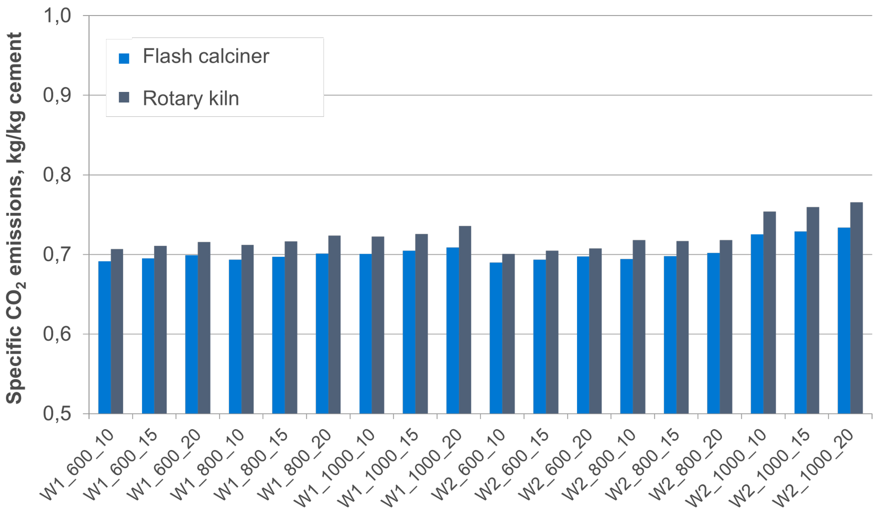

Figure 2: Specific CO_2 emissions of the production of composite cements with 20 % calcined clay depending on the calcination temperature (600, 800 and 1000 °C) and different raw material moisture (10, 15 and 20 wt.%), order of designation: clay_temperature_moisture

Taking into account the specific CO_2 emissions of 0.842 kg/kg Portland cement clinker (ECRA (2017)), the specific CO_2 emissions for the production of a composite cement with 20 wt.% calcined clay were calculated (cf. Figure 2) for raw clays with 10, 15 and 20 wt.% moisture. The specific CO_2 emissions of the production of such a cement are therefore around 0.7 kg/kg cement. Due to the high CO_2 contribution of the clinker compared to the clay used, the influence of the clay composition, moisture and calcination temperature is almost negligible. The influence of the selected calcination technology also moves into the background.

The differences between the simulated calcination technologies became more apparent with increasing calcined clay proportion in cement. The CO_2 emissions of the production of a cement with for example 40 wt.% calcined clay were between about 0.5 and 0.6 kg CO_2/kg cement at a calcination temperature up to 800 °C, depending on the calcination technology and raw material moisture.

4. Conclusions

The calcination of two different Calcite containing clays in a rotary kiln and in a flash calciner was simulated. The following conclusions can be stated:

- As the CO_2 emissions caused by the calcination of clays consist of combustion-related and raw material-related CO_2, different Calcite contents of the clays have a particularly large influence on the amount of CO_2 emitted at temperatures higher than 800 °C. Therefore, for materials containing carbonate, a firing temperature of more than 800 °C is not recommended with regard to CO_2 emissions.
- Depending on the calcination technology the emissions for both clays were between about 0.12 and 0.17 kg CO_2/kg calcined clay for calcination at 600 °C and between about 0.14 and 0.22 kg CO_2/kg for calcination at 800 °C.
- Under the assumptions made, the calcination process in the flash calciner is more efficient than calcination in the rotary kiln, both in terms of energy and CO_2 emissions. Beside other factors a significant difference is made by the waste heat losses, which are higher in the rotary kiln. Taking into account a more intensive use of waste heat or integration of clay calcination into the clinker production process, the disadvantages of the rotary kiln shown in the model can be significantly reduced.
- For the production of cements with 20 wt.% calcined clay the influences of clay mineralogy, moisture and calcination temperature as well as the calcination technology used are neglectable due to the high CO_2 footprint of Portland cement clinker. The specific CO_2 emissions of such a cement are about 0.7 kg/kg cement.

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