

CO₂ and energy savings potential of ternary cements with calcined clay and blast furnace slag

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Abstract

In view of the challenges of decarbonisation of the cement industry, the use of low-clinker ternary cements especially with calcined clays is becoming increasingly important [1]. The combination of Portland cement clinker (K), ground granulated blast furnace slag (S) and calcined clay (Q) in ternary cements is very promising in terms of cement and concrete properties.

In this study the CO₂ footprint of such cements as well as the energy required for their production was determined over a wide range of cement compositions systematically for the first time. The results were related to the strength development of the cements and the mineralogical composition as well as the moisture of the used clays. Compared to an OPC

(CEM I 42.5), both the CO₂ and energy saving potentials for the production of ternary KSQ cements are between 25 and 55 % respectively, depending on the cement composition.

1. Introduction

In view of the challenges of decarbonisation in the cement and concrete industry, the use of low-clinker ternary cements, in particular with calcined clays, is becoming increasingly important [1]. According to the European standards EN 197-1 [2] and EN 197-5 [3], calcined clays can be used in several types of cements. Especially in ternary cements, which consist of two reactive main constituents in addition to Portland cement clinker, such as ground granulated blast furnace slag (S), fly ash or calcined clay (Q), synergies between the main constituents can be used to improve their performance [e.g. 4, 5]. Systematic investigations of KSQ-cement properties, e.g. water demand and compressive strength, in combination with concrete durability aspects, e.g. resistance to carbonation, chloride and freeze-thaw attack, were carried out for the first time in [6].

The ecological assessment of common composite cements is possible due to sufficient data on CO₂ emissions and energy requirements for the production of their main components such as slag and others [7]. For the calcination of clays of different compositions, these data are given in [8]. There, both the clay composition and the production process were taken into account in order to assess the CO₂ emissions and energy required for the production of clay containing cements. The results presented here complete the lack of data for KSQ cements.

2. Materials and Methods

2.1. Materials

For the production of the KSQ-cements one OPC without minor constituents and two calcined clays (Clay A and B) were used. Clay A was a kaolinitic clay with about 15 wt.% Magnetite, Clay B was an illitic clay with about 40 wt.% Quartz. After the analyses of the raw clays by means of X-ray fluorescence analysis (XRF) and X-ray diffraction analysis (XRD), Clay A was calcined at 700 °C and Clay B at 800 °C in a chamber furnace for 30 minutes respectively. The calcined clays were ground to the same fineness in a laboratory ball mill and analysed concerning their pozzolanic reactivity acc. EN 197-1 (amount of reactive SiO₂) and ASTM C 1897-20 (heat of hydration and bound water). The analyses results are given in [6].

An average quality ground granulated blast furnace slag (S) was used as the third cement component (RRSB position parameter $x' = 21,86$, RRSB slope $n = 0,95$). 3.5 wt.% natural anhydrite was used for slag sulphatisation.

2.2. Methods

In order to be able to investigate a wide range of different cement compositions, Design of experiments (DoE) was applied by using the statistical software Minitab®. Figure 1 shows the cements defined in EN 197-1 and EN 197-5 in the ternary diagram clinker (K) – ground granulated blast furnace slag (S) – calcined clay (Q). The 16 cement compositions produced in this project acc. the DoE test plan were marked in orange in the range outlined in red and consisted of 20 to 90 wt.% OPC, 5 to 59 wt.% S and of 5 to 49 wt.% Q. Laboratory cements were produced homogeneously by intensive mixing of the respective components. Their compressive strength acc. EN 196-1 after 28 days of hydrations are given in [6].

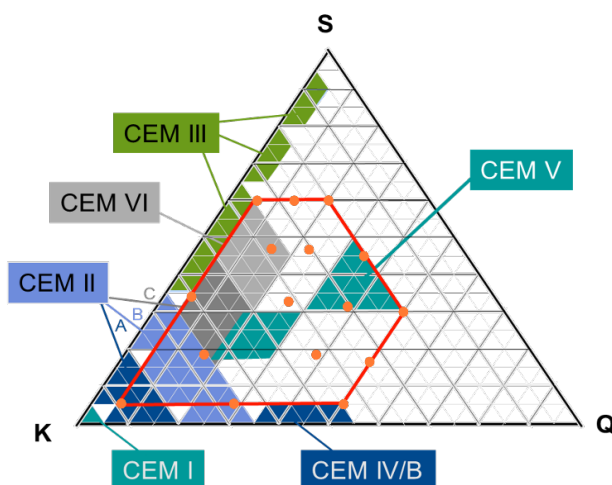


Figure 1 Area of investigated cements compositions acc. to EN 197-1 and EN 197-5 (red); mixture design of DoE, tested cement compositions are marked with orange dots

The data determined in [8] for flash calcination were used to determine the CO₂ emissions and energy required for the production of the KSQ cements. The data are summarised in Table 1 and show that the calcination of clay A, although it is calcined at a lower temperature than clay B, results in higher CO₂ emissions and higher specific energy consumption than clay B. This is due to the fact that clay A contains significantly more clay minerals than clay B and therefore it requires more energy per kg of raw clay to decompose it.

Table 1 Data basis for the calculations of CO₂ emissions and energy requirement of the production of KSQ cements [7, 8, 9]

	Clay A		Clay B		S	K
	10 % mo- isture	20 % mo- isture	10 % mo- isture	20 % mo- isture		
CO ₂ emissions, kg/kg	0,139	0,182	0,1	0,137	0,1	0,832
Thermal energy , kJ/kg	1489	1943	1044	1446	-	3352
Electrical energy , kJ/kg	36	36	36	36	180	180
Total energy , kJ/kg	1525	1979	1080	1482	180	3532

The calculations refer to two different moisture contents (10 and 20 wt.%). The data for the required grinding energy for all input materials as well as for the granulated blast furnace slag (S) and the clinker (K) were taken from [7, 9]. It was assumed that the clinker was ground to a fineness of 4000 cm²/g acc. Blaine and the granulated blast furnace slag to a fineness of 3000 cm²/g acc. Blaine. The energy required for the grinding of the calcined clay has been in line with that of limestone.

3. Results and Discussion

3.1. CO₂ emissions

The CO₂ emissions from the production of KSQ cements are mainly determined by the amount of clinker in the cements. The influence of the clay's moisture was of minor importance. Therefore, the following results only refer to moisture contents of 10 wt.%.

Figure 2 shows that the CO₂ emissions for the production of the majority of KSQ cements in the test area were between 0.3 and 0.6 kg CO₂ /kg cement. Due to the comparable CO₂ footprints of granulated blast furnace slag and calcined clay (see Table 1), there was hardly any difference in the CO₂ emissions of the KSQ cements whether granulated blast furnace slag or calcined clay was substituted.

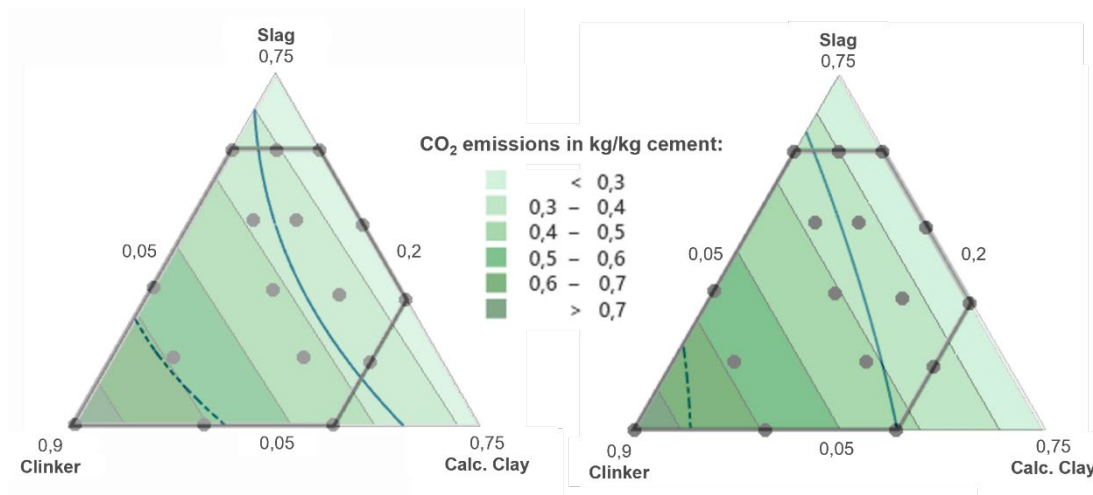


Figure 2 Specific CO₂ emissions of the production of KSQ cements in kg/kg cement with clay A (left) and clay B (right), each with 10 % moisture in the raw material, the solid and dashed blue lines mark the area of strength class 42.5 according to EN 197-1

In Figure 2, the specific CO₂ emissions of the KSQ cements have been overlaid with their 28-day strengths. The range of strength class 42.5 is marked by the two blue lines (solid line: 42.5 MPa, dashed line 62.5 MPa). The production of a KSQ cement of strength class 42.5 would therefore release between approx. 0.35 and 0.6 kg CO₂ per kg cement. A clear difference between the two clays in terms of CO₂ emissions in relation to the strength after 28 days is only recognisable in the area of higher strengths (see area around the dashed blue line in Figure 2). This is because more clinker has to be used to reach the same compressive strength, when using the less reactive clay B.

Assuming that the production of a CEM I cement of strength class 42.5 with 95 wt.% clinker released about 0.79 kg CO₂ / kg cement (0.832 kg CO₂ · 0.95), the CO₂ saving potential in the production of KSQ cements of this strength class would be between approx. 25 and 55 %, depending on the cement composition.

3.2. Energy requirement

With regard to the energy requirement for the production of KSQ cements, a clear effect was recognisable, which was attributable to the mineralogical composition and also to the moisture content of the raw clays. In Table 1 it can be seen that the energy required for drying and calcining the investigated clays increased by more than 400 kJ/kg when the moisture content of the clays was increased from 10 to 20 %.

However, the influence of the moisture content of the raw clays fades into the background when considering the grinding energy for the production of KSQ cements. Both clinker and granulated blast furnace slag are used in much larger quantities and are more difficult to grind than calcined clays. Figure 3 illustrates, that the total energy required for the production of KSQ cements was less than 2500 kJ/kg cement for most of the cement compositions analysed. If the substitution rate of the clinker was below 30 %, cement production usually requires more than 2500 kJ/kg cement. As only the grinding energy has to be considered when

using blast furnace slag as a cement constituent (see Table 1), a high proportion of slag has a particularly positive effect on the specific energy requirement of KSQ cements.

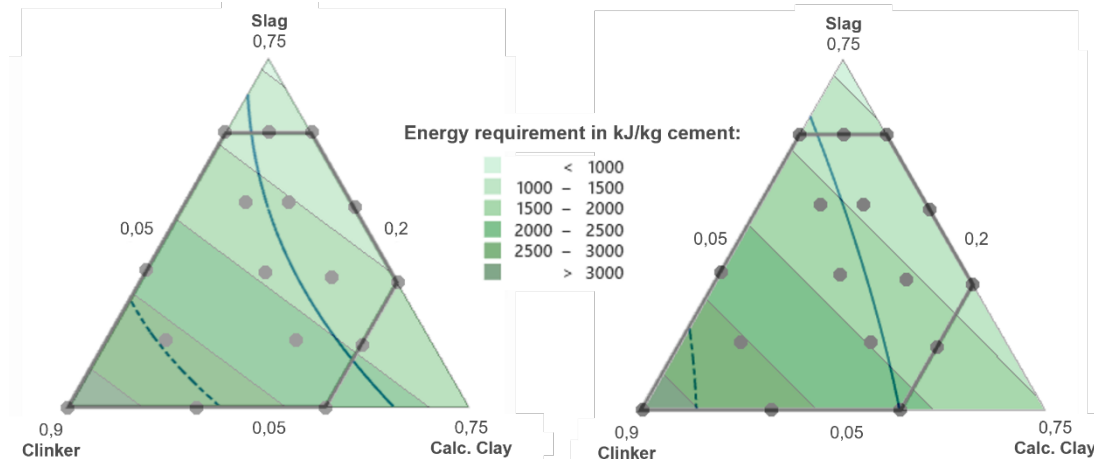


Figure 3 Energy requirement for the production of KSQ cements in kJ/kg cement with clay A (left) and clay B (right), each with 10 % moisture in the raw material, the solid and dashed blue lines mark the area of strength class 42.5 according to EN 197-1

In Figure 3, the specific energy requirements for the production of KSQ cements are also superimposed on their 28-day strength. As in Figure 2, the range of strength class 42.5 is marked by the two blue lines (solid line: 42.5 MPa, dashed line 62.5 MPa). It is shown that the production of a KSQ cement of strength class 42.5 with calcined clay A would be associated with a specific energy requirement of between 1500 and 2500 kJ/kg cement. This corresponds to a saving of around 25 to 55 % compared to a CEM I 42.5 (95 wt.% clinker) with a specific energy requirement of about 3355 kJ/kg ($3532 \text{ kJ/kg} \cdot 0,95$).

The higher quality of calcined clay A had a positive effect on the energy requirement of the cements produced with it, even though calcination required more energy. The reason is that the higher reactivity of clay A compared to clay B allows substituting more clinker for a given compressive strength of the KSQ cement.

4. Summary and Conclusions

Using data from [8] both the CO₂ footprint of cements containing granulated blast furnace slag and calcined clay (KSQ) as well as the specific energy requirement for their production were modelled.

As the CO₂ emissions from the production of KSQ cements are mainly determined by the amount of clinker in the cements, the influence of the moisture content of the raw clays was of minor importance.

The CO₂ emissions for the production of most of the investigated KSQ cement compositions were between 0.35 and 0.6 kg CO₂ /kg cement. Therefore, the CO₂ saving potential in the production of KSQ cements of strength class 42.5 would be between approx. 25 and 55 % compared to a CEM I cement, depending on the cement composition.

The total energy required for the cement production was less than 2500 kJ/kg cement for most of the cement compositions analysed. Compared to a CEM I 42.5 the production of a KSQ cement of the same strength class saves about 25 to 55 % energy, depending on the composition.

Acknowledgement

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