Durability of concretes with ternary cements

Simone Elisabeth Schulze | Joerg Rickert, VDZ Technology gGmbH, Düsseldorf

Abstract

The production of cements with calcined clay is becoming increasingly important for the cement industry for ecological and economic reasons. Especially the combination of the cement constituents granulated blast furnace slag (S) and calcined clay (Q) next to Portland cement clinker (K) is very promising in terms of cement properties, durability and CO_2 saving potential. Due to a lack of knowledge and experience, such KSQ cements have not yet been produced in Europe.

With the help of design of experiments and statistical evaluation, both the influence of the cement composition and the reactivity of the clinker and calcined clays used on the cement and concrete properties were determined. For this purpose, a total of 64 different cement compositions consisting of at least 20 wt.% clinker (two different qualities), a maximum of 59 wt.% granulated blast furnace slag and a maximum of 49 wt.% calcined clay (two different qualities) were investigated.

It could be shown that in a wide range of compositions, the production of KSQ cements of strength class 42,5 acc. EN 197-1 is possible, whereby the water demand of the cements was mainly determined by the amount of calcined clay. Most of the corresponding concretes exhibited a high resistance to carbonation, chloride and freeze thaw attack.

Keywords

Ternary cements, Calcined clay, Blast furnace slag, Compressive strength, Water demand, Durability, Concrete, Carbonation resistance, Chloride resistance, freeze-thaw attack

1 Introduction

In view of the challenges of decarbonisation of the cement and concrete industry, the use of low-clinker ternary cements especially with calcined clay is becoming increasingly important [1]. According to the European standard EN 197-1 [2], calcined clays can be used in 8 different types of cement. Additionally, the new EN 197-5 [3] specifies the composition of further low-clinker cements. Accordingly calcined clays can be used in CEM II/C-M cements. But due to a lack of experience, ternary cements with calcined clay and ground granulated blast furnace slag (GGBFS) as main constituents (CEM VI) have not yet found their way into the new EN 197-5, although this combination in particular is very promising in terms of its cement properties and concrete performance as well as its CO_2-saving potential. However, cements with calcined clays are not yet produced on an industrial scale in Europe. This means that there are no practical construction experiences with these cements.

Especially in ternary cements, which in addition to Portland cement clinker consist of two other reactive main constituents such as GGBFS, fly ash or calcined clay synergies between the main

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constituents can be used to improve their performance [e.g. 4, 5]. The in context of global decarbonisation expected decline in available quantities of fly ashes [6] and the high availability of clays will necessitate the production of ternary cements with calcined clays and GGBFS. Therefore, systematic investigations on the cement properties as strength development and water demand are needed in timely manner. Usually, negative effects on workability of mortars and concretes were observed with increasing proportion of calcined clay in cements [7, 8]. In addition, the type of clay mineral also has an influence on the water demand of calcined clay cements, especially metakaolin can cause a high water demand [9].

With regard to the durability of ternary cements with granulated blast furnace slag and calcined clay (KSQ), there are no published test results so far. In [5,10] it could be shown that the combination of granulated blast furnace slag and siliceous fly ash in ternary cements (KSV) leads to well performing cements and concretes of high durability. Due to the comparable pozzolanic properties of calcined clay and fly ash, it is to be expected that KSQ cements also show good durability properties. This could be confirmed for the first time in this research, where their resistance against carbonation, chloride and freeze thaw attack was determined.

2 Materials and Methods

2.1 Materials

For the production of the KSQ-cements two OPC (CEM_A and CEM_B) without minor constituents and two calcined clays (Clay A and B) were used (see Table 1). The Portland cements (OPC) differed in their phase composition and their fineness. OPC B was more reactive than OPC A. 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 XRF and 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 SiO_2) and ASTM C1897-20 [11] (heat of hydration and bound water).

An average quality ground granulated blast furnace slag (GGBFS) 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.

Table 1 Chemical-mineralogical and physical parameters

Parameter	Unit	OPC_A	OPC_B	Clay_A	Clay_B
Position parameter x' (RRSB)	µm	21.84	10.69	20.57	20.18 **
Slope n (RRSB)	-	0.88	0.93	0.88 *	0.90 **
Water demand acc. Puntke [13]	%	39.6	42.4		
Alite acc. Bogue (XRF)		55.1	65.8		
Belite acc. Bogue (XRF)		18.8	15.5		
C3A acc. Bogue (XRF)		6.7	7.0		
C4AF acc. Bogue (XRF)		12	4.2		
Kaolinite (XRD)				70 – 80	15
Illite/Muskovite (XRD)				< 5	40
Quartz (XRD)				< 1	40
Feldspar (XRD)				< 2	< 3
Magnetite (XRD)				ca. 15	-

Hematite (XRD)				< 2	< 3
Glass content acc. ZKG					
Reactive SiO2 acc. EN 197-1 [2]				37.3 *	15.9 **
Bound water acc. ASTM C1897-20 [11]	g/100g			10.4 *	3.9 **
Heat of hydration after 3 days acc. ASTM C1897-20 [11]	J/g			620 *	154 **
Heat of hydration after 7 days acc. ASTM C1897-20 [11]				663 *	162 **

* calcined at 700 °C and ground in a ball mill

** calcined at 800 °C and ground in a ball mill

2.2 Methods

2.2.1 Design of experiments

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) – 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 % OPC, 5 to 59 % GGBFS and of 5 to 49 % calcined clay.

Using one GGBFS, two OPC and two calcined clays therefore resulted in 4 combinations, so that 64 (4 x 16) different cements were investigated. The respective raw materials were weighed out according to the specifications of the test plan and the cements were produced homogeneously by intensive mixing.

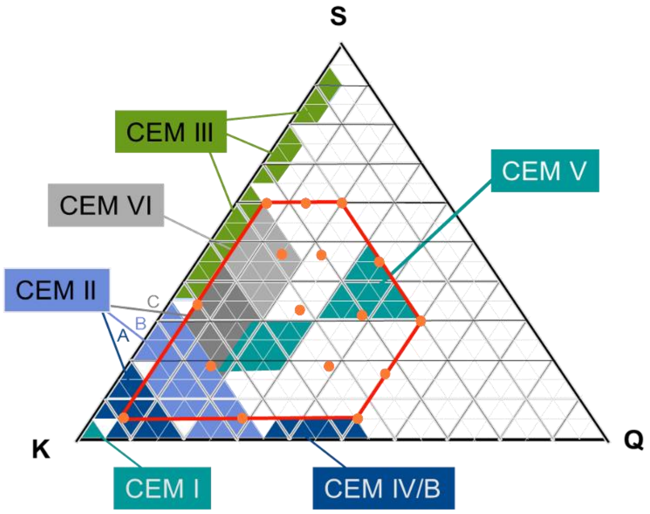

Figure 1 Area of investigated cements compositions acc. to EN 197-1 and EN 197-5 (red); mixture design of DoE, tested cement compositions are marked with orange dots

2.2.2 Cement properties

The cements were investigated concerning their compressive strength acc. EN 196-1 [12] at 28 days of hydration and their water demand. To minimize the consumption of test material the water demand was determined according to the method of Puntke [13]. This water demand characterizes the saturation water demand of fine, low-cohesion particles. The method is based on the observation that a finely ground material can be reproducibly compacted by light impacts to a material-specific packing density as soon as the water content is sufficient to saturate the dense particle structure. The absolute water demands acc. Puntke are different to the water demands acc. EN 196-3, but the values are comparable. The water demands acc. Puntke of the OPC's used are given in Table 1.

2.2.3 Durability tests

Investigations on the durability of concretes were carried out with 6 different cements, which represented the investigated area well. Their composition is shown in Figure 2. In order to minimise the number of different concretes and the amount of cement required for them, all tests were carried out on a concrete with 300 kg/m^3 cement (w/c = 0.60, quartzitic aggregates, grading curve AB 16).

The carbonation resistance was tested according to EN 12390-10 [14] on concrete beams after 7 days wet curing stored at 20 °C and 65 % relative humidity over a period of up to one year.

The chloride resistance was determined according to [15] by a chloride migration measurement at the age of 28 and 91 days (after seven days of wet curing). A voltage of 15 V was applied. In addition, the chloride diffusion was determined according to EN 12390-18 [16].

The freeze thaw resistance was determined via the scaling quantity in the cube test according to CEN/TS 12390-9 [17].

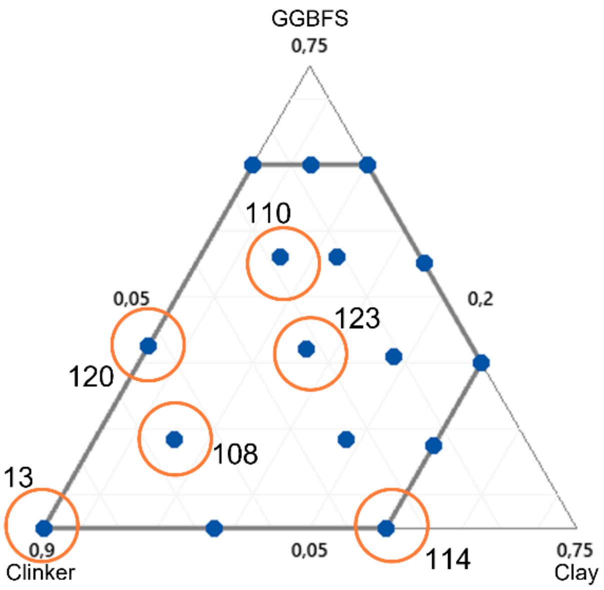

Figure 2 Composition of the cements (orange) used for durability tests in the ternary diagram (Clinker, Slag, Clay)

3 Results

3.1 Compressive strength

Figure 3 shows the results of the model calculation of the compressive strength after 28 days of hydration as a function of the content of the three cement components clinker, GGBFS and calcined clay as well as of the reactivity of both the calcined clay and the used OPC. Bottom left: low clinker reactivity (OPC A) and low calcined clay reactivity (clay B); bottom right: high clinker reactivity (OPC B) and low calcined clay reactivity (clay B); top left: low clinker reactivity (OPC A) and high calcined clay reactivity (clay A); top right: high clinker reactivity (OPC B) and high calcined clay reactivity (clay A). The area of compressive strengths from 42,5 MPa (blue line) to 62,5 MPa (dotted blue line) is marked white, so that this area comprises all cements with the strength class 42,5 and 52,5.

A high influence of the clinker quality on the 28-day compressive strength could observed. This can be seen in the clear difference between the diagrams on the left (less reactive clinker) and those on the right (more reactive clinker). Nevertheless, since the pozzolanic reaction had already started at that hydration time, the influence of the clay quality on the compressive strength was also visible. This is shown by the shift of the strength ranges towards higher strengths when comparing the lower contour diagrams (lower clay reactivity) with the two upper ones (higher clay reactivity). Therefore, the influence of the clay quality on the 28-day strength of the cement becomes higher by the use of clinker of lower reactivity.

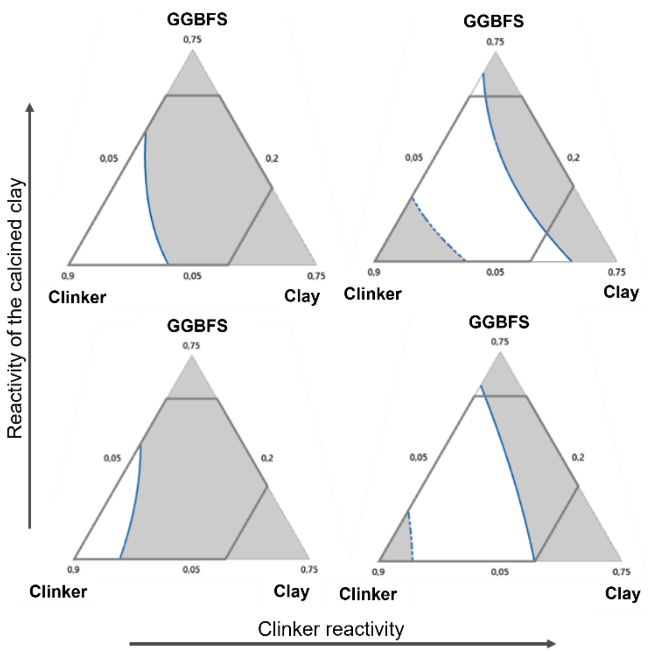

Figure 3 Ternary diagrams with the results of the model calculation of the compressive strength at 28 days; white: compressive strength from 42,5 to 62,5 MPa

3.2 Water demand

Figure 4 shows results of the model calculation of the water demand acc. Puntke as a function of the content of the three cement components clinker, GGBFS and calcined clay as well as of the reactivity of the calcined clay and the fineness of the OPC (OPC B finer than OPC A). Tested cement compositions are marked with black dots. From blue to green the water demand rises. Information concerning the estimated regression coefficients for the terms and the model summary are given in [18].

The water demand according to Puntke was over wide ranges between 40 and 46 %, depending on the fineness of OPC used. It is clearly visible that the water demand, as expected, is mainly influenced by the amount of calcined clay in the system. When comparing the corresponding diagrams below with those above, it is noticeable, that there is hardly any difference between the cements with the two different calcined clay qualities. This is due to the almost identical fineness of the two calcined clays (see Table 1). This behaviour also shows that the different composition of the calcined clays, especially their metakaolin content, has no influence on the water demand of the investigated systems.

In contrast, the influence of the clinker fineness on the water demand of the cements is clearly recognisable and becomes apparent when comparing the two left-hand diagrams with the two right-hand diagrams. Larger quantities of the used GGBFS have a positive effect on the water demand according to Puntke, the corresponding cements showed the lowest water demand in each case.

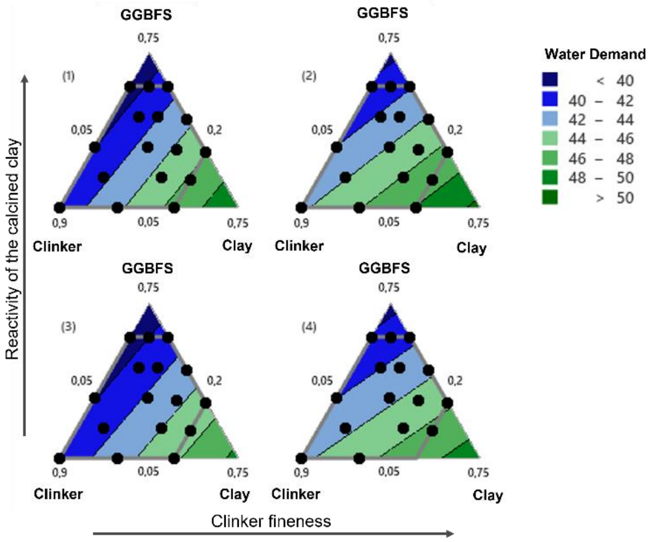

Figure 4 Results of the model calculations for the water demand of the cements in % [18]

3.3 Durability

3.3.1 Carbonation resistance

Figure 5 shows the carbonation depths of the tested concretes depending on the test age. Due to the variation of the concrete composition these data are not directly comparable with carbonation depths determined according to [14].

As expected, the concretes could be divided into two groups with regard to their carbonation resistance. The concretes with CEM II cements (113, 108 and 120) showed only low carbonation depths in the range of up to 3 mm even after 180 days. The concretes with cements containing less than 50 wt.% clinker (110, 114 and 123) showed significant higher depth of carbonation. This behaviour was to be expected according to the results from [19]. The stronger carbonation can be attributed to the fact that due to the lower clinker content in the cements, only little portlandite was available as a buffer against carbonation, which was also consumed by the pozzolanic reaction of the calcined clay. Additionally, the reaction products of the blast furnace slag and the calcined clay are lower in calcium than the CSH phases formed by the clinker, which reduces the resistance to carbonation.

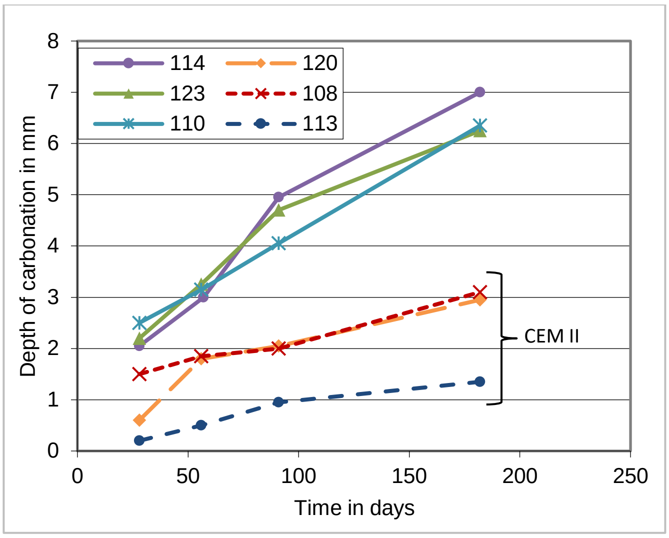

Figure 5 Depth of carbonation acc. EN 12390-10 of the tested concretes

3.3.2 Chloride migration resistance

Figure 6 shows that all concretes tested had good or very good chloride migration resistances. With chloride migration coefficients below $5 \cdot 10^{-12} m^2/s$, the concretes with the cements 108 (CEM II/B), 120 (CEM II/C), 114 (CEM IV/B) and 110 (CEM VI) had an excellent chloride migration resistance. In addition, the concretes with the clay-rich cements 114 (CEM IV/B) and 123 (CEM X) showed a clear pore-blocking effect, which is typical for cements containing pozzolanic materials. This effect was also observed in the other concretes with the exception of the CEM II/A concrete (113), whereby these concretes already showed good chloride resistance after a test age of 35 days, which speaks for a relatively dense pore structure already at this earlier test time.

The results of the chloride diffusion measurement underline the good properties of the tested concretes with regard to chloride resistance.

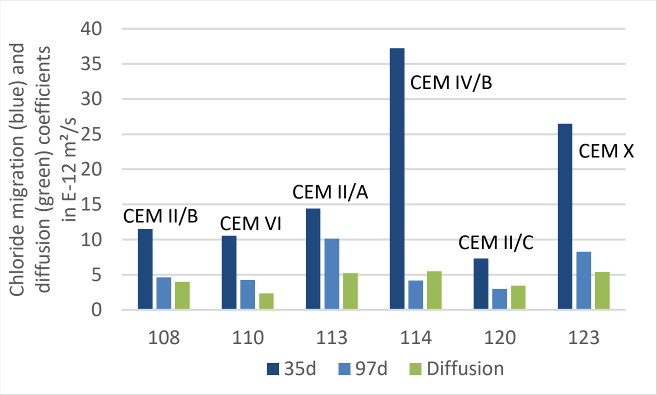

Figure 6 Chloride migration coefficients of concretes with clay containing cements after 35 and 97 days (blue markers) and chloride diffusion coefficients (green markers)

3.3.3 Resistance against freeze thaw attack

The results of the cube test according to CEN/TS 12390-9 are shown in Figure 7. It can be clearly seen that the tested concretes can be divided into three groups. In the first group are the concretes with CEM II cements (113, 108 and 120), which, as expected, showed very little scaling. In the second group are the concretes with the CEM VI cement (110) and the CEM X cement (123), both cements with a clinker content below 50 wt.%. Despite this low clinker content, the concretes show scalings below 5 wt.% after 100 freeze-thaw cycles and are thus clearly below the limit value of the BAW criterion (defined by Federal Waterways Engineering and Research Institute).

Only the concrete with the CEM IV/B cement (114), which had a calcined clay content of 50 wt.%, showed a clearly higher scaling and was clearly above the limit value after 100 freeze-thaw cycles. This is mainly due to the late beginning of the pozzolanic reaction, resulting in a rather porous microstructure at the start of the freeze thaw cycles. It hast to be pointed out, that a low clinker content in the KSQ cements is not a general problem for the freeze thaw resistance. This is shown by the good performance of the concretes with the CEM VI (110) and CEM X (123) cements, both of which have slightly lower clinker contents than the comparable CEM IV/B cement (114).

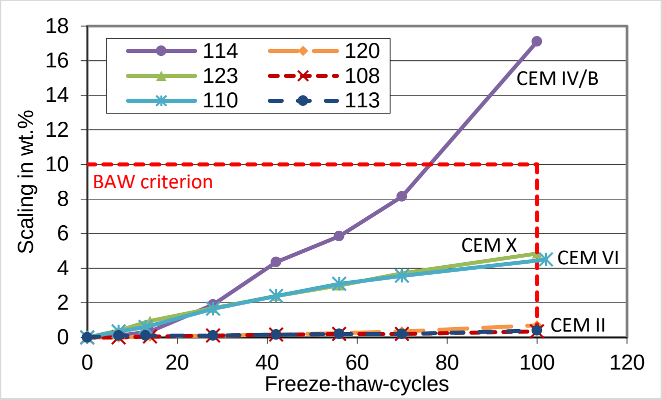

Figure 7 Scaling of concrete cubes during freeze thaw test

4 Summary and conclusions

A wide composition range of standardised and non stan-dardised ternary cements containing calcined clay and ground granulated blast furnace slag (GGBFS) was systematically investigated and statistical evaluated regarding the water demand and the compressive strength by use of design of experiments (DoE).

It can be stated that with the use of a clinker of high reactivity and/or a high-quality calcined clay, the production of KSQ cements of strength class 42,5 and higher is possible over a wide composition range, even outside the current standardised compositions. In this respect, the production of high performing CEM VI cements with granulated blast furnace slag and calcined clays (CEM VI (S-Q)), which are not standardised yet, is possible.

The water demand of the ternary cements depends in general on the calcined clay content and the fineness of the cement components. The reactivity of the calcined clay, on the other hand, has a minor influence on the water demand. Larger quantities of GGBFS have a positive effect on the water demand.

In addition to the determination of cement properties, investigations on the durability of concretes were carried out with 6 different cements.

Concretes with CEM II cements showed only low carbonation depths. The concretes with cements containing less than 50 wt.% clinker carbonated to a greater extent. This behaviour is due to the fact that in these concretes only little Portlandite is available and that the CSH formed by blast furnace slag and calcined clay has lower Calcium contents.

Nearly all concretes tested show a good or very good resistance against chloride migration, chloride diffusion and – with one exception (tested CEM IV/B) – also a high resistance against freeze thaw attack.

5 Acknowledgement

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