Durability of composite cements with calcined clay

Composite cements are clinker efficient and play an important role in reducing CO_2 emissions from cement manufacturing. To assure their correct application in concrete, their performance in concrete has to be demonstrated, especially with regard to durability under different concrete exposure conditions. As part of a long-term research programme, such cements made of different calcined clays were used in conventional concrete mixtures and tested for their resistance to carbonation, chloride migration, frost and frost-de-icing salts.

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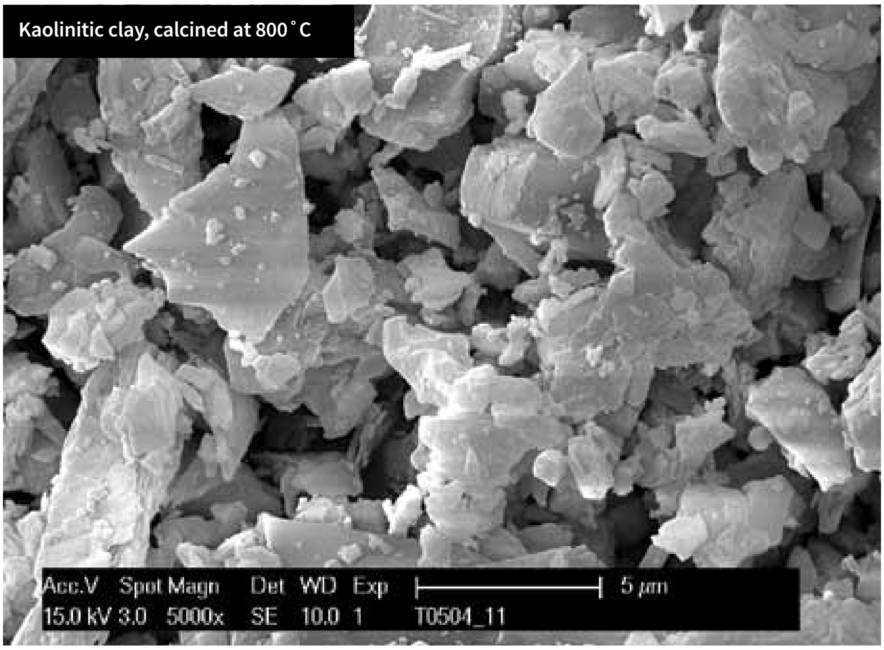
Clays and in particular calcined clays have long been known as building materials. While suitable clays are available worldwide in large quantities, they show strong differences in composition and regional availability. For example, Europe has a tradition in using calcined clays in cement and the current European cement standard EN 197-1 provides for calcined clays as a main constituent (Q) in cement. The use of suitable clays depends on the clay's quality and availability. Unfortunately, since high-quality clays such as pure kaolinitic and illitic ones are limited in regional availability and/or used for other purposes than cement making, the market share of these respective cements is low in Europe (2016: ~2.5 per cent of CEM IV, including Q, D, P, V, W). Easily-available clays, such as those from overburden, show low ceramic properties but can nevertheless be taken into consideration for economic as well as ecological reasons for composite cement production. Because most investigations so far were performed on clays with high ceramic quality, VDZ investigated the performance of several calcined clays as a cement main constituent. The kaolinitic, illitic and chloritic clays used in these investigations were of explicitly low ceramic qualities, as is the case in many cement plant quarries, in particular in Europe. Suitable calcination conditions on laboratory scale led to appropriate pozzolanic reactive compounds (silica and alumina), resulting in acceptable strength developments when used in cements with a clinker substitution of 20 and 40 mass-per cent.[1] Nevertheless, some loss in performance (eg, early strength) could not be avoided, as the clay qualities were not on the level used in other investigations.[2,3] However, further research showed that there is a good potential to further optimise the interaction of clinker, calcined clay and the sulphate carrier.[4,5] Details on clay compositions, calcination and cement properties could also be found in Pierkes et al (2015) and Schulze et al (2015).

Kaolinitic clay, calcined at 800˚C



In this study cements with different calcined clays were produced on laboratory scale, using substitution rates of 20 and 40 mass-per cent (CEM II/A-Q, CEM IV/A-Q). Concrete mixtures as used in tests for European Technical Approvals (ETA) were produced with these cements and tested for their resistance to carbonation, chloride migration, frost and frost-de-icing salts.

Test methods

Table 1 shows the concrete compositions and respective test standards used for the durability tests, as well as the range of compressive strengths obtained after 28 days.

Results

Table 1 shows that concretes with useful compressive strength up to C 35/45 according to EN 206-1 could be achieved. Only the air-entrained concrete with CEM IV/A-Q (40 mass-per cent calcined clay) did not reach the strength required by EN 206 for such an exposure.

Table 1: Concrete test parameters and results of concrete compressive strength

Parameter	Concrete Type A	Concrete Type B
Composition • Cement content (kg/m³) • W/c ratio • Aggregate grading • Air entraining agent (AEA)	 300 0.60 ≈B16 No	 320 0.50 ≈AB16 AEA – air voids: 4.5-5.5 vol%
Compressive strength	EN 12390-3	EN 12390-3
Resistance to carbonation	EN 12390-10	-
Resistance to chloride migration	Chloride migration test (following NT Build 492 (11.99) [6]	-
Resistance to frost	Cube frost (CEN/TS 12390-9)	-
Resistance to frost-de-icing salts	-	CDF (CEN/TS 12390-9)
Compressive strength range CEM II/A-Q at 28 days (MPa)	37-52 (requirement according to EN 206-1: ≥C 25/30, passed)	38-50 (requirement according to EN 206-1: ≥C 30/37, passed)
Compressive strength range CEM IV/A-Q at 28 days (MPa)	27-45 (requirement according to EN 206-1: ≥C 25/30, passed)	28 (requirement according to EN 206-1: ≥C 30/37, passed)

The workability of the concretes was strongly influenced by the type of calcined clay and calcination temperature. Kaolinitic clays, calcined at temperatures of about 600-700˚C to maximise their pozzolanic reactivity, show a very high specific surface and a wide water demand range (~36-40 per cent). Concretes using this clay type in cement demonstrated a loss in workability that sometimes must be compensated with a superplasticiser, which itself could strongly be absorbed by the calcined clay compound.[7] Illitic clays that need higher calcination temperatures up to sintering conditions (eg, 1200˚C) did not show this effect. In single cases the concrete workability could even be slightly improved depending on the particle size distribution and content of fines.

Carbonation

A crucial aspect of concrete durability is the resistance against carbonation, which should be given special attention for cements with extended use of pozzolanic main constituents. In Figure 1 the depth range of carbonation obtained from concretes with and without use of CEM II/A-Q and CEM IV/A-Q is shown. As expected, the carbonation resistance is somewhat lower compared to CEM I (OPC) but is not outside the range as typically shown by blastfurnace cements or Portland limestone cements. Further improvement can be achieved with extended curing and lower water-to-cement (w/c) ratios.

Chloride migration

As known from experience with eg, fly ash cements, pozzolanic cement, main constituents can decrease the chloride migration coefficient in concrete. Figure 2 shows that this does not occur in all cases. Kaolinitic clays show comparably low coefficients after just 35 days (Mix A, Mix B) and predominantly illitic clays show a more delayed pozzolanic effect with a strong decrease of the coefficient at 98 days (Mix C, Mix D). Higher amounts of calcined clays with less-reactive calcined clays, ie higher impurities of quartz and carbonates (Mix E, Mix F), do not reduce the migration coefficient at all due to a higher porosity of the concrete microstructure.

Frost and frost-de-icing salt

For the broader use of calcined clay composite cements in concretes under

Figure 1: ranges in depth of carbonation of concretes with CEM II/A-Q (20 mass-per cent calcined clay) and CEM IV/A-Q (40 mass-per cent calcined clay), related to typical CEM I and blastfurnace cement

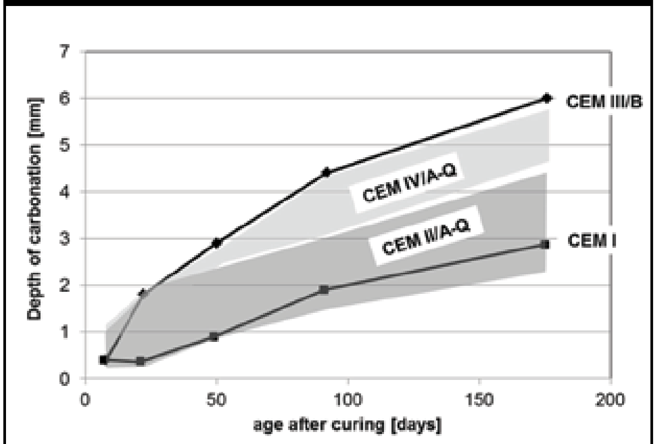


Figure 2: chloride migration coefficient of concretes with different CEM II/A-Q (20 mass-per cent of different calcined clays to A to F), related to typical CEM I and Portland limestone cement results, age: 35 or 98 days

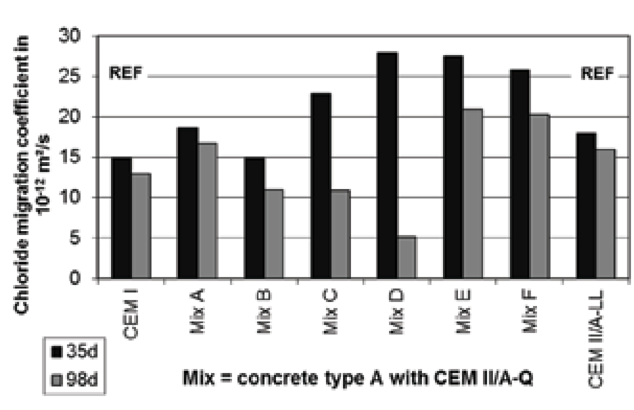


Figure 3: scaling ranges of concretes with CEM II/A-Q and CEM IV/A-Q in cube test (according to EN CEN/TS 12390-9), compared to typical CEM I concrete and limit value

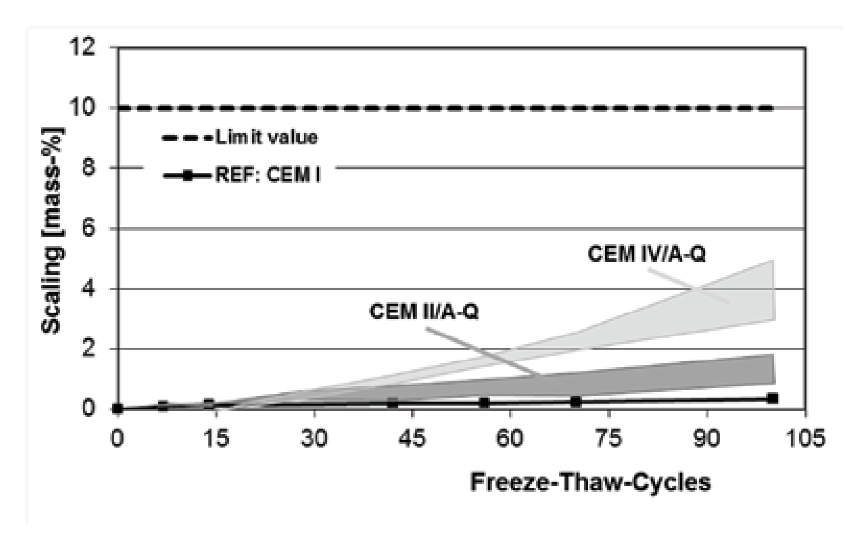
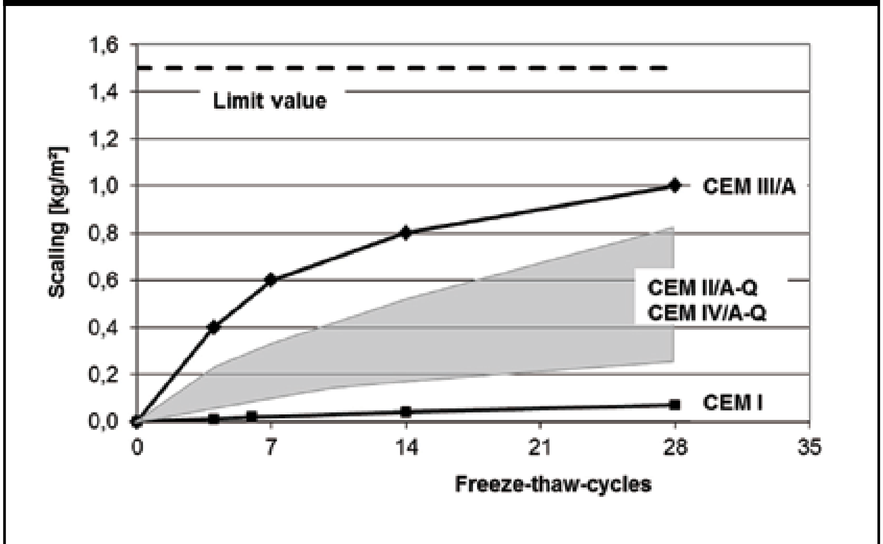


Figure 4: scaling ranges of concretes (type B) with CEM II/A-Q and CEM IV/A-Q in CDF test (according to EN CEN/TS 12390-9), compared to CEM I and CEM III/A concrete and the limit value



frost exposure a suitable frost resistance of the respective concretes will be required. Figure 3 displays the results of the cube test, described in CEN/TS 12390-9. In this test, concrete cubes are subjected to 100 frost-thaw cycles, and a loss in weight of up to 10 mass-per cent is accepted to pass the test ("high frost resistance"). All CEM II/A-Q tested in the research project showed a final loss in weight below two mass-per cent, indicating a suitable frost resistance. Even the tested CEM IV/A-Q did not exceed a weight loss of five mass-per cent and passed this test successfully.

To prove the frost-de-icing salt resistance of a concrete according to CEN/TS 12390-9, a capillary suction, de-icing agent and freeze-thaw (CDF) test was performed. The concrete specimen surfaces were immersed in a salt solution and exposed to 28 frost-thaw cycles. To pass the test, a scaling of less than 1500g/m^2 concrete surface is required. Figure 4 shows the results of several calcined clay concretes subjected to the CDF test. All concretes tested showed a scaling in a range known from eg, blastfurnace slag cements and passed the criteria of a scaling of less than 1500g/m^2.

Conclusions

The acceptance of new composite cements with calcined clays on the European market depends on their performance in concrete, especially with respect to durability. Within a research project, VDZ tested concretes made of CEM II/A-Q and CEM IV/A-Q laboratory cements with respect to durability, for instance resistance to carbonation, chloride migration and frost as well as frost-de-icing salt exposure.

To ensure an appropriate workability of the concretes that could be affected by strong increases in the water demand of specific types of calcined clays in the cement, corrective measures in the calcination technique, particle size distribution of the clays/cements and the use of superplasticisers can be required.

The durability tests showed that the performance of the investigated CEM II/A-Q and CEM IV/A-Q cements is comparable to cements with other substitution compounds such as limestone, blastfurnace slag or fly ash. As the pozzolanicity of calcined clays which do not mainly consist of kaoline becomes more effective with higher hydration age, a further increase of the concrete performance is expected with ongoing hydration time. Some loss in cement performance at early hydration times may have to be accepted. ■

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