POZZOLANIC CEMENT WITH TEMPERED PHONOLITE ROCK POWDER

PUZZOLANZEMENT MIT GETEMPERTEM PHONOLITH-GESTEINSMEHL

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SUMMARY

Regarding the further development of clinker-reduced cements, a CEM IV/B-Q pozzolanic cement with temperered phonolite as a main constituent was investigated. Strength development and durability tests were carried out.

ZUSAMMENFASSUNG

Hinsichtlich der Fortentwicklung klinkerreduzierter Zemente wurde ein Puzzolanzement CEM IV/B-Q mit getempertem Phonolith als Hauptbestandteil untersucht. Hierbei wurden Prüfungen zur Festigkeitsentwicklung und zur Dauerhaftigkeit durchgeführt.

1. INTRODUCTION

In order to reduce CO_2 emissions and energy consumption in the production of binders, low-clinker or clinker-reduced cements are being produced for the market increasingly. For this purpose, most frequently used is ground granulated blast furnace slag, fly ash and calcium carbonate filler aggregate. Pozzolans also offer great potential as clinker substitutes. With a view to further reducing clinker content, a pozzolanic cement CEM IV/B-Q was developed, which has a clinker content of between 45% and 50%. In order to prove the cement's suitability for use in concrete and reinforced concrete in accordance with DIN EN 206-1 in conjunction with DIN 1045-2 for all exposure conditions (except XF4) as well as for bored pile walls in accordance with DIN EN 1536/ DIN SPEC 18140, extensive tests were carried out at the Otto-Graf-Institute of the MPA University of Stuttgart.

The present publication also compares the results of these investigations with earlier investigations on binder mixtures composed of CEM II/B-M cements and tempered phonolite powder (GG).

2. PHONOLITE

Phonolite is a volcanic rock. Tempering at around 380°C increases the reactivity with calcium hydroxide. The reason is explained by the dehydration of the zeolite during tempering. During hydration with calcium hydroxide, tetra-calcium aluminate trisulfate hydrate is formed [1].

The phonolite rock is mined at the quarry, crushed and tempered in the rotary kiln at Bötzingen on the Kaiserstuhl.

The phonolite rock powder has so far been used as a natural tempered pozzolan (Q) as the main component of cement (CEM II/B-Q) according to DIN EN 197-1 as well as a concrete additive type II "Hydrolith F200" (ETA-05/0213 [2]) [3].

3. INVESTIGATIONS ON THE PHONOLITE CEMENT

3.1 Cement constituents

The tempered phonolite rock is grounded together with the clinker and the sulphate into cement in a combination of vertical roller mill and ball mill at the manufacturing plant at Bötzingen. The tested cement mixture was composed of the following main constituents (sulphate-free stated): 44% portland cement clinker and 56% tempered phonolite.

3.2 Cement properties

The Blaine fineness was 594 m²/kg with a determined density of 2.84 g/cm³. The Na_2O equivalent of the investigated cement mixture was 5.5 m.-%, the SO_3 content determined by wet chemistry was 1.6 m.-%. The chemical constituents determined with the full chemical analysis by x-ray fluorescence analysis (containing ignition loss) are shown in Table 1.

Table 1: Cement constituents of the CEM IV/B-Q-Cement

Constituents in M.-%	
SiO_2	35,3
Al_2O_3	12,1
Fe_2O_3	4,1
MgO	1,2
CaO	36,6
K_2O	2,9
Na_2O	3,6
ignition loss	3,3

According to DIN EN 196-3 the CEM IV cement had a water demand of 31.0 %, the initial set was 180 min, and the elongation measure for the volume stability was 0 mm.

3.3 Mortar tests

The mortar compressive strengths of the prisms were determined according to DIN EN 196-1 at ages of 2, 7, 28 and 90 days. The two binder mixtures used here for comparison with the CEM IV cement consisted of a CEM II/B-M (T-LL) cement and a CEM II/B-M (V-LL) cement respectively. In the production of the standard mortar according to DIN EN 196-1, the CEM II/B-M cement was replaced by 25% tempered phonolite powder (GG) in each case. The two binders produced in the laboratory had the following compositions in %:

- CEM II/B-M (T-LL) with GG: K/T/LL/GG = 49/12/14/25
- CEM II/B-M (V-LL) with GG: K/V/LL/GG = 54/9/9/25, minor additional constituents 3%

The compressive strengths at 7, 28 and 90 days of age are available for these two binder mixtures.

The mortar compressive strengths of the two binder mixtures and the CEM IV cement are shown in Table 2. The mortar compressive strengths show a similar strength curve between the two binder combinations and the CEM IV cement.

Table 2: Mortar compressive strengths

Test age in d	Mortar compressive strength in MPa		
	CEM ll/B-M (T-LL) 42,5 N with GG	CEM II/B-M (V-LL) 32,5 R with GG	CEM IV
2	-	-	15,3
7	28,0	25,6	32,1
28	44,6	42,8	47,5
90	48,3	51,5	52,9

4. CONCRETE TESTS

Regarding the durability, investigations were carried out on carbonation behaviour and freeze-thaw resistance. Furthermore, investigations were carried out on the CEM IV cement regarding resistance to chloride penetration and resistance to wear stress.

4.1 Carbonation

The tests on the carbonation behaviour were carried out on fine concrete prisms with the dimensions 40 mm x 40 mm x 160 mm. Here, mortars with a water-cement ratio of w/c = 0.50 with a binder content of 450 g per mixture and a gravel aggregate with a grading curve A8/B8 were produced. The prisms were pre-aged in water at (20±2) °C for 7 days. Subsequently, the samples were stored in the climatic room at (20±2) °C and (65±5) % RH. This storage time corresponds to the main storage.

Fig. 1 relates the carbonation depths after 140 days of main storage with the compressive strength after 7 days of pre-storage and classifies the carbonation depth in the assessment background according to Annex B of DIN CEN/TR 16563 [4].

The investigated mortars are within the admissible range below the limit function at a pre-storage of 7 days.

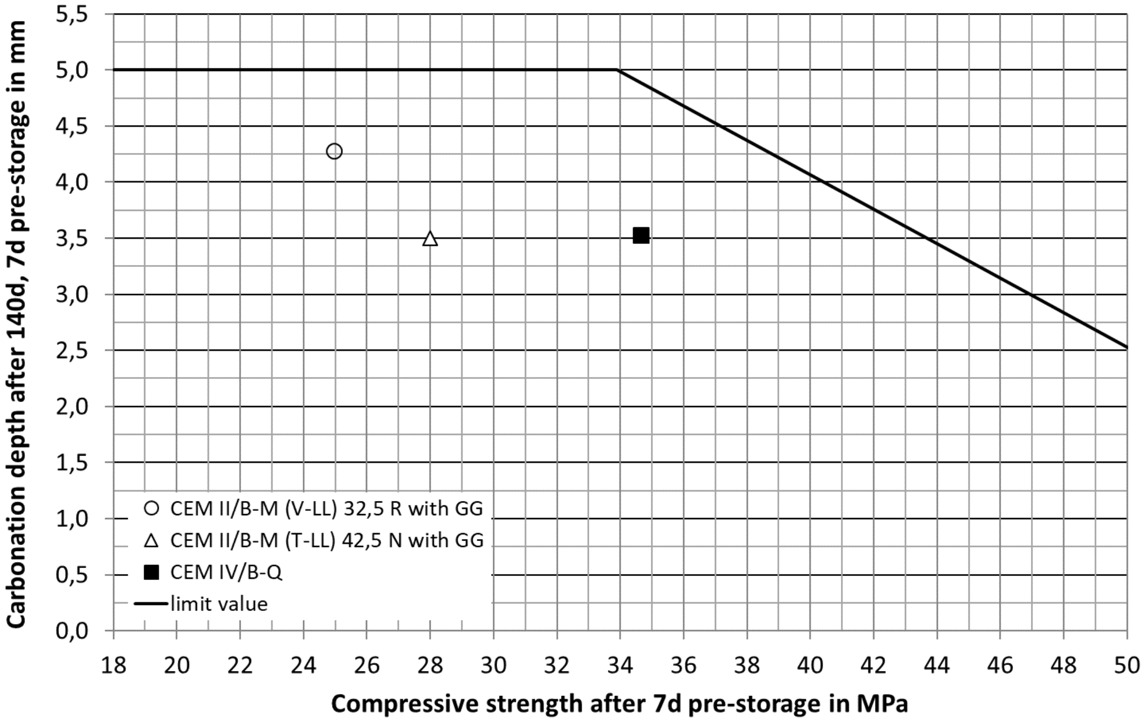

Fig. 1: Classification in the assessment background according to Annex B in [4]

4.2 Concrete compressive strength and frost resistance

The tests for freeze-thaw resistance (CIF method) were carried out according to the BAW leaflet "Frostprüfung von Beton" (MFB) [5]. The mix composition of the concretes was 320 kg/m³ binder with a w/c ratio of 0.50 and a grading curve A16/B16. For the concrete with the CEM IV cement, a further series of tests was carried out with a slightly lower water-cement ratio of w/c = 0.45. Since this concrete was produced with the same cement paste content for comparability, the cement content here is 340 kg/m³.

The concrete compressive strength tested with this mixture was determined according to DIN EN 12390-3 at the age of 28 days on cubes with an edge length of 150 mm (Fig. 2). The cubes were stored in water up to the age of 7 day and then in the standard climate of 20/65. The values are between 46 MPa and 54 MPa, and 56 MPa for the mixture with a slightly lower w/c ratio.

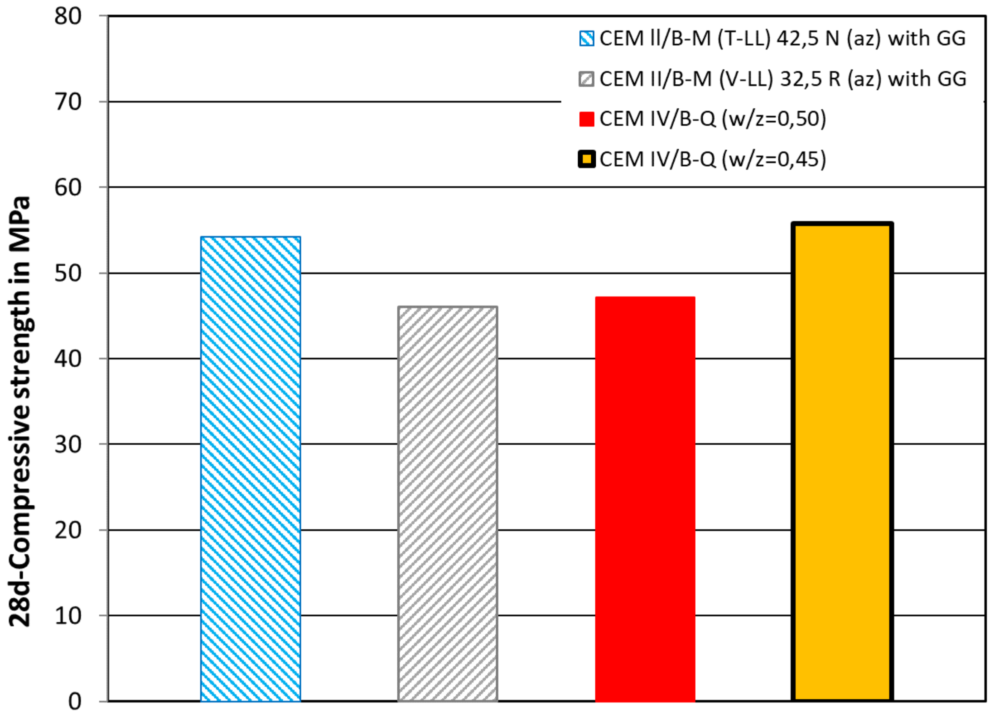

Fig. 2: Concrete compressive strength at 28 d

The manufactured concrete cube specimens were stored in water at (20±2) °C up to 7 days and then in standard climate 20/65 for 21 days. At the age of 7 days, the specimens were sawn to the standard height of 70 mm. After 28 days, the test specimens, sealed on the side surfaces with aluminium foil with butyl adhesive, were placed with the test side in demineralised water for capillary suction. Afterwards, the test specimens were stored in the freezer.

The temperature cycle of a freeze-thaw cycle (FTC) lasted 12 hours. Within a FTC, the temperature in the freezer is lowered at a constant cooling rate of 10 K/h according to a predefined temperature curve, kept at -20 °C for 3 h and then thawed again at a heating rate of 10 K/h.

The dynamic modulus of elasticity and the dried mass of the weathered components of the concrete were determined up to 28 freeze-thaw cycles (FTC). The dynamic modulus of elasticity is a measure of the internal structural damage caused by the freeze-thaw attack. The relative modulus of elasticity is calculated for each test specimen from the change in the sound velocity in relation to the sound velocity at the beginning of the CIF test. As an additional criterion, the weathering on the exposed test side was determined.

For each test series, the mean values of the relative elastic moduli are shown in Fig. 3 and the mean values of the determined weathering amounts (cumulated) are shown in Fig. 4.

Fig. 3 shows that the relative moduli of elasticity for all binders is above the evaluation criterion of 75 %. However, for the additional criterion of weathering (Fig. 4), the sample of the CEM IV cement with w/c = 0.50 is above the limit value of 1.0 kg/m². By lowering the w/c value to w/c = 0.45, this criterion could also be met.

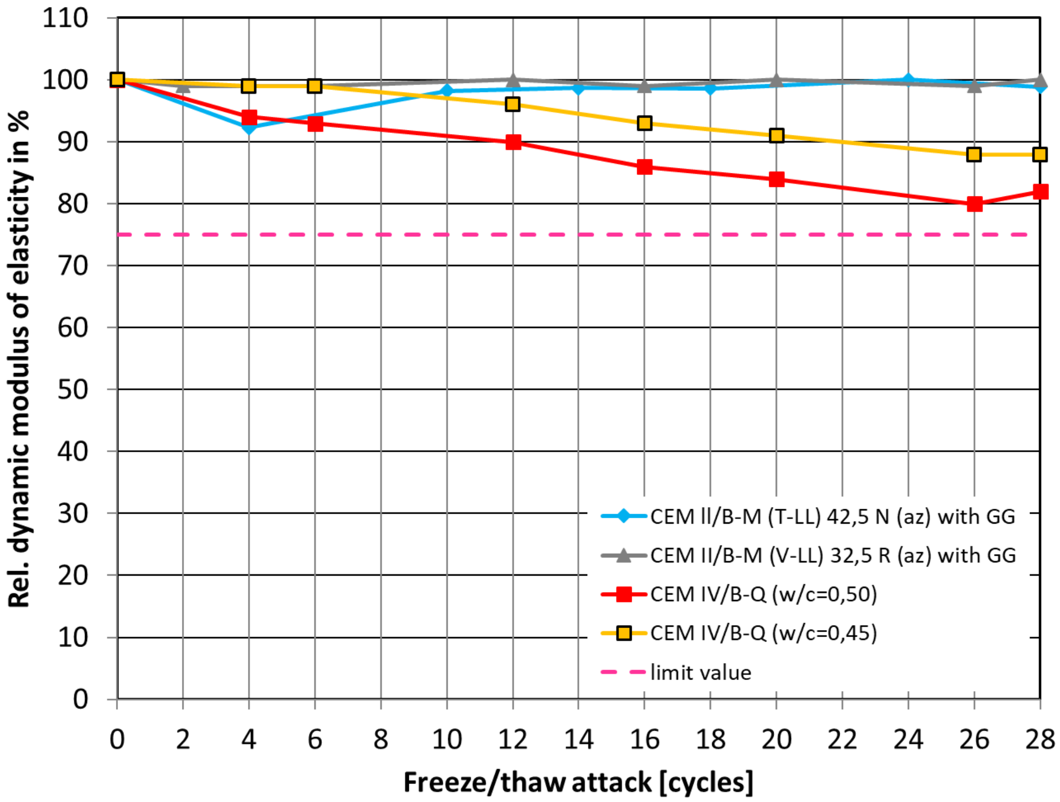

Fig. 3: Relative dynamic modulus of elasticity at CIF-Test

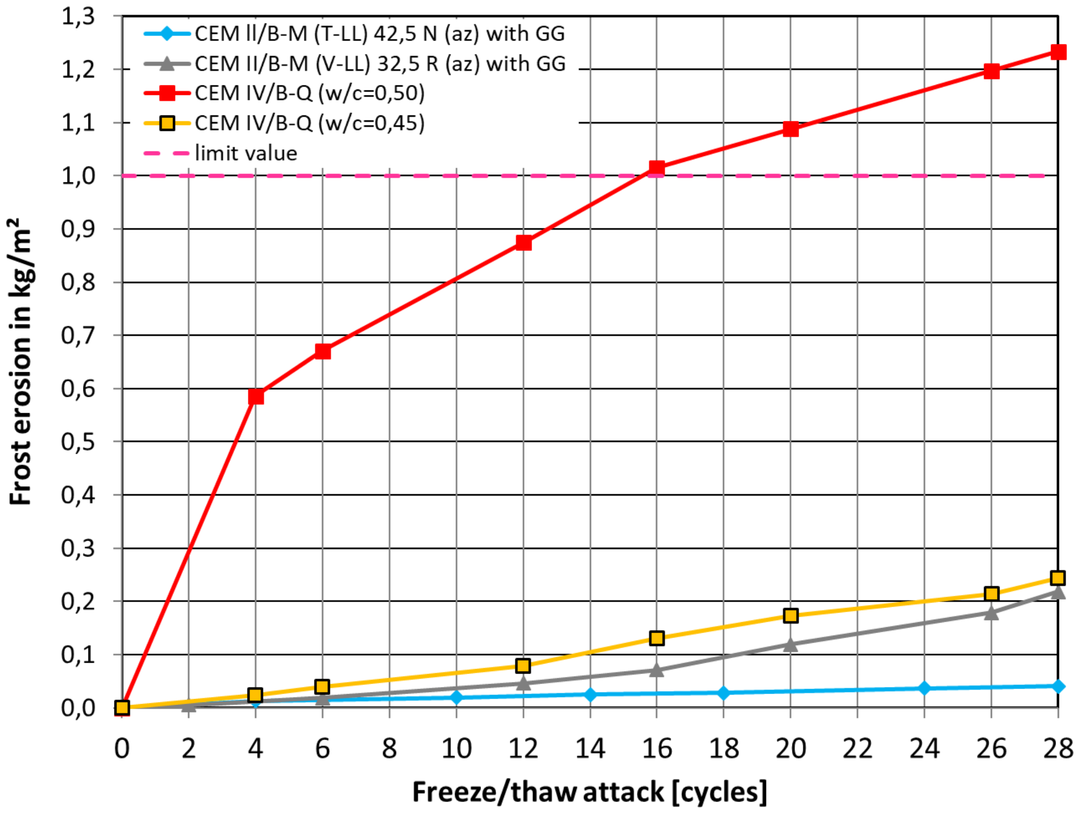

Fig. 4: Defrosting process of concrete at CIF-Test

4.3 Chloride penetration resistance

The resistance of the concrete to chloride penetration was determined with the chloride migration test according to the BAW leaflet "Chloride Penetration Resistance" (MCL) [6] after 35 and 97 days of water storage at (20±2) °C. A 10% sodium chloride solution was used as the electrolyte solution for the test.

Cylindrical samples were obtained from the concrete cubes by drilling them out and shortening them to the required dimensions. For the experiment, the outer surfaces of the cylinders were sealed with a fabric tube so that ion exchange with the surrounding electrolyte solution was only possible via the base surface (surface facing the cathode). A stainless steel electrode was arranged on the upper surface, via which a constant voltage was regulated with the help of a potentiostat. A chloride-free potassium hydroxide solution was applied to the upper sample surface facing the anode. The test voltage was set to 30 V. Due to the applied test voltage, ions of the electrolytes and the pore water migrated to the oppositely charged electrode, i.e. chloride ions migrated through the sample to the anode.

After the test, the samples were split and sprayed with an indicator to visually determine the penetration depth of the chloride ions. The so-called migration coefficient D_{Cl} is derived mathematically from the penetration depth according to the method given in the BAW leaflet [6].

After 35 days, the investigations resulted in an average chloride migration coefficient D_{Cl} of $3.6 \cdot 10^{-12}$ m²/s. After 97 days, a D_{Cl} value of $2.5 \cdot 10^{-12}$ m²/s was obtained. This represents a high resistance to chloride penetration.

4.4 Wear test resistance

The determination of the wear resistance was carried out using the grinding wheel according to Böhme in accordance to DIN 52108. Test specimens were made of fine concrete with the test mixture CEM IV/B-Q and with a comparative cement CEM II/B-Q. The mixtures were each composed of 900 g cement, 450 g water (w/c = 0.50) and 2700 g aggregate (grading curve A8/B8). After stripping, the specimens were stored under water at (20±2) °C for 27 days. Afterwards, the samples were dried at 105 °C until mass constancy. The wear resistance was determined at the age of 40 days.

The test specimens were subjected to a total of 16 test cycles (352 turns). The used abrasive was specified to DIN 52108. The thickness loss was determined at 9 specified measuring points per test specimen after 16 test cycles.

Furthermore, the mass loss was determined after 4 test periods each. Table 3 shows the sum of the individual mass losses after 352 turns as the mean value of three test specimens. The respective volume loss, related to an area of 50 cm², was determined from the two measurement parameters.

Table 3: Wear test resistance after 352 turns (mean value of three specimens)

	thickness loss Δl (mean value of 9 measuring points)	volume loss ΔV_D	mass losses Δm (sum after 352 turns)	volume loss ΔV_G
CEM IV/B-Q	1,96	9,8	19,6	9,6
CEM II/B-Q	1,78	8,9	18,3	8,8

The tests provided comparable results to a CEM II/B-Q cement approved for the exposure condition XM.

5. SUMMARY AND OUTLOOK

In the investigations, the suitability of the present pozzolanic cement for the production of concrete and reinforced concrete was proven. In the meantime, a general technical approval for the pozzolanic cement has been obtained from the DIBt [7].

The pozzolanic cement CEM IV/B-Q (az) may be used for exposure conditions X0, XC, XD, XS, XA, XM and XF1 to XF3. The cement is approved for strength classes 32.5 R and 42.5 N. For the exposure classes XF2 and XF3, separate composition requirements apply. In this case the maximum permissible w/c ratio is set at 0.45 with a minimum cement content of 340 kg/m³.

Further investigations into the sulphate resistance are currently being carried out at the Otto-Graf-Institute. The aim is to extend the approval as an SR cement.

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