CALCIUM CARBONATE FILLER AGGREGATE WITH REDUCED $CACO_3$ CONTENT

KALKSTEINMEHL MIT VERMINDERTEM $CACO_3$-GEHALT

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SUMMARY

With regard to the resource-conserving use of raw materials for the production of concrete, the durability of calcium carbonate filler aggregate with a reduced $CaCO_3$ content was investigated. The investigations were carried out according to the principles of the concept of equivalent concrete performance for the combination with a CEM I cement. The aim was that the cement content and the water-cement ratio could be taken into account in the concrete composition.

ZUSAMMENFASSUNG

Hinsichtlich einer ressourcenschonenden Verwendung von Ausgangsstoffen für die Herstellung von Beton wurden Untersuchung zur Dauerhaftigkeit von Kalksteinmehlen mit vermindertem $CaCO_3$-Gehalt durchgeführt. Die Untersuchungen erfolgten nach den Grundsätzen des Konzepts der gleichwertigen Betonleistungsfähigkeit für die Kombination mit einem CEM I Zement mit dem Ziel der Anrechenbarkeit bei der Betonzusammensetzung auf den Zementgehalt und den Wasserzementwert.

1. INTRODUCTION

Regarding to the resource-saving utilisation of existing limestone deposits, studies have been carried out in the past on dolomite-containing calcium carbonate filler aggregate (in the following referred to as filler aggregate) for use in concrete. In a vdz IGF research project [1], the suitability in principle of dolomite-containing limestone with a lower $CaCO_3$ content than the 75 % by mass previously specified in DIN EN 197-1 [2] for use as a cement constituent was demonstrated. This led to an extension of the limestone filler aggregates to be used as a cement raw material in the new DIN EN 197-5 [3] and DIN EN 197-6 [4]. These standards authorise the use of limestone (LL, L) if the calcium carbonate content ($CaCO_3$) is at least 40 % by mass and the sum of the calcium carbonate content and magnesium carbonate content ($CaCO_3$ and $MgCO_3$) is at least 75 % by mass.

In addition to its use as a cement component, limestone filler aggregate is used as a type I concrete additive in concrete in accordance with DIN EN 12620 [5], e.g. to improve rheological properties or as a filler. Furthermore, in Germany the use of limestone filler aggregate for the production of concrete is possible in accordance with the principles of the concept of equivalent concrete performance in the sense of section 5.2.5.3 of DIN EN 206-1 [6] via a general technical approval (abZ).

The basis for this is an European Technical Document EAD 260048-00-0301 [7], which regulates limestone filler aggregate with special properties over and above DIN EN 12620 [5]. These additional requirements relate to the $CaCO_3$ content ≥ 75 % by mass, the clay content ≤ 1.20 g/100 g, the TOC content ≤ 0.20 % by mass and the chloride content ≤ 0.10 % by mass. Based on this EAD, European Technical Approvals (ETA) can be issued for limestone filler aggregates of certain origins.

Earlier approval tests have already proven the suitability of a limestone filler aggregate for a manufacturer from southern Germany. This limestone filler aggregate may be added to the cement content and the water-cement ratio according to DIN EN 206-1, section 5.2.5.1 [6] in the concrete composition.

At the Otto Graf Institute of the MPA University of Stuttgart, investigations have been carried out now into the use of dolomite-containing limestone filler aggregate with a low $CaCO_3$ content of ≤ 75 % by mass. The aim was to extend the usable limestone filler aggregates in concrete according to the concept of equivalent concrete performance in analogy to the above-mentioned ETA or abZ.

This publication presents the results of tests on limestone flours with different $CaCO_3$ contents.

2. EXPERIMENTAL PROGRAMME

2.1 Limestone filler aggregate

The present test programme comprises the testing of four limestone flours (type LL) from two different manufacturers CCF-1 and CCF-2 (Table 1). Each of the limestone filler aggregate tested originates from a limestone deposit in southern Germany. They are produced during the manufacture of crushed aggregates and fulfil the requirements for a filler in accordance with DIN EN 12620 [5].

Table 1: List and designation of the analysed limestone filler aggregate

Abbreviation	Material	Type	Manufacturer	Note
CCF-2-65	Calcium carbonate filler	shell limestone	2	65 % $CaCO_3$
CCF-1-70			1	70 % $CaCO_3$
CCF-1-75			1	78 % $CaCO_3$
CCF-2-80			2	80 % CaCO3

The filler aggregate showed differences in CaO and MgO content in particular, but the Na_2O equivalent and fineness also varied. The calcium carbonate content ($CaCO_3$) calculated from the calcium oxide content varied from 65 to 80 % by mass. The sum of calcium carbonate content and magnesium carbonate content ($CaCO_3$ and $MgCO_3$) was ≥ 75 % by mass for all four fillers.

The other results of the physical properties are listed in Table 2 and those of the chemical components in Table 3.

Table 2: Particle density and specific surface of the limestone filler aggregates

	CCF-2-65	CCF-1-70	CCF-1-75	CCF-2-80
Particle density ^{A} [g/cm³]	2.76	2.75	2.80	2.73
Specific Surface ^{B} [cm²/g]	3820	3400	2880	4590
^{A} determined in accordance with DIN EN 1097-7 [11] ^{B} determined in accordance with the air permeability method (Blaine) specified in DIN EN 196-6 [12]				

Table 3: Chemical components of the limestone filler aggregates in % by mass

	CCF-2-65	CCF-1-70	CCF-1-75	CCF-2-80
SiO_2	13.7	14.0	8.3	9.4
TiO_2	0.2	0.2	0.1	0.1
Al_2O_3	4.5	4.5	2.5	3.0
Fe_2O_3	1.6	1.6	1.1	1.1
MgO	6.5	4.5	4.5	3.6
CaO	36.8	39.0	43.6	44.7
K_2O	2.0	1.9	0.9	1.2
Na_2O	0.1	0.1	0.1	0.1
Loss on ignition	34.5	34.1	38.6	37.7
Na_2O-Equivalent [A]	1.4	1.4	0.7	0.8
$CaCO_3$ [B]	65	70	78	80
$MgCO_3$ [C]	14	9	9	7
$\Sigma(CaCO_3+MgCO_3)$	79	79	87	87
Clay content [D]	0.5	0.5	0.3	0.3
TOC [E]	0.17	0.16	0.09	0.14
Chloride [F]	0.01	< 0.01	< 0.01	< 0.01

[A] Na_2O-Equivalent calculated from the total content of alkalis determined in accordance with DIN EN 196-2 [8]
[B] calculated from the CaO content of the full chemical analysis using XRF
[C] calculated from the MgO content of the full chemical analysis using XRF
[D] determined according to DIN EN 933-9 [9]
[E] Total organic carbon (TOC) content, determined according to DIN EN 13639 [10]
[F] Content of water-soluble chloride ions, determined according to DIN EN 196-2 [8]

2.2 Binder production

The use of limestone filler aggregates in accordance with general building inspectorate approval may be used in concrete if the combination consists of up to 18 % limestone filler aggregates by mass and at least 82 % CEM I by mass. A portland cement CEM I in accordance with DIN EN 197-1 [2] of strength class 42.5 R and higher must be used.

To verify the equivalent concrete performance, the tested binder combinations for the mortar and concrete tests each consisted of 82 % of a commercially available CEM I 42.5 R cement and 18 % of the respective limestone filler aggregate. Only when testing the binder properties was a less favourable ratio of cement to filler aggregate tested.

As part of the tests, the mortar compressive strengths of the binder combinations were tested in comparison to the mixture with 100 % CEM I 42.5 R cement (reference mixture).

2.3 Concrete production

The following durability tests were carried out on the concrete: Compressive strength, freeze-thaw resistance (CIF), carbonation behaviour and chloride penetration resistance. Round aggregates (gravel, sand) from the institute's stocks were used for the concrete mixtures.

The mix composition of the concretes was 320 kg/m³ binder with a water-cement ratio of 0.50 in relation to the total binder content and an aggregate composition of A16/B16 in accordance with DIN 1045-2, Annex L [13]. The coarse aggregates met the requirements for aggregates for exposure class XF3 in accordance with DIN 1045-2 [13].

The fine concrete for the carbonation test was produced with a water-cement ratio of 0.50 in relation to the total binder content with a binder content of 450 g per mixture and 1350 g of a gravel aggregate with a grading curve A8/B8 in accordance with DIN 1045-2, Annex L [13]. Concrete admixtures were not used.

Table 4 shows the results of the fresh concrete properties. It can be seen that the results differ only slightly from each other and therefore the influence of the limestone filler aggregates tested here on the fresh concrete is almost the same.

Tab.4: Fresh concrete properties

	CEM I + CCF-2-65	CEM I + CCF-1-70	CEM I + CCF-1-75	CEM I + CCF-2-80
Fresh concrete density [kg/m³]	2360	2390	2390	2370
Air content [Vol.-%]	1.8	1.2	1.2	1.3
Degree of compactability [-]	1.41	1.41	1.30	1.42

3. PRESENTATION OF THE RESULTS

3.1 Binding agent properties

The binder mixtures and the reference cement were tested for water demand, setting behaviour and soundness in accordance with DIN EN 196-3 [14]. In accordance with the specifications of EAD 260048-00-0301 [7], the composition of the binder mixtures for determining the water demand and setting times consisted of 75 % CEM I cement and 25 % limestone filler aggregate. For the determination of the room resistance, a composition of the binder with 70 % CEM I cement and 30 % limestone filler aggregate was specified.

The results (Table 5) show that the influence of the limestone filler aggregate used on the tested properties compared to the reference cement can be rated as low. This applies both to the range of filler aggregate tested here with regard to fineness from 2880 to 4590 cm²/g and to the $CaCO_3$ content of 65 to 80 % by mass.

Table 5: Initial setting time and soundness of the binder mixtures

	CEM I	CEM I + CCF-2-65	CEM I + CCF-1-70	CEM I + CCF-1-75	CEM I + CCF-2-80
Water demand [A] [%]	27.0	27.5	27.5	26.5	27.5
Initial setting time [min]	150	125	160	135	125
Soundness (expansion) [mm]	0.0	1.5	0.0	0.0	0.0
[A] Water content required to set the standard stiffness, based on the cement or binder mixture					

3.2 Mortar testing

The mortar compressive strengths of the prisms were determined in accordance with DIN EN 196-1 [15] at 2, 7, 28 and 90 days (Fig. 1).

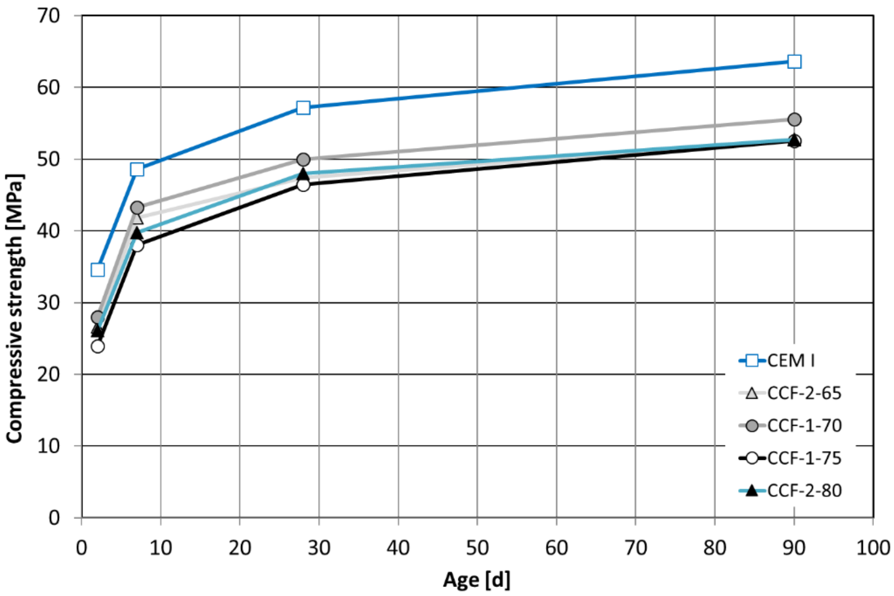

Fig. 1: Compressive strength of the mortars

The 2-day values of the binder mixtures were between 23.9 and 28.0 MPa, after 7 days between 38.0 and 43.3 MPa, after 28 days between 46.4 and 50.0 MPa and after 90 days between 52.6 and 55.6 MPa. The compressive strengths of the reference mixture were 34.6 MPa after 2 days, 48.6 MPa after 7 days, 57.2 MPa after 28 days and 63.6 MPa after 90 days. Compared to the reference cement, the decrease in strength of the binder combinations after 28 days corresponds to between 13 and 18 %. The initial strengths determined after 2 days and the standard strengths after 28 days were all within the required range for the specified strength class 42.5 R in accordance with DIN EN 197-1 [2].

3.3 Concrete strength

The concrete compressive strength of the concrete mixes was determined in accordance with DIN EN 12390-3 [16] at an age of 28 days on cubes with an edge length of 150 mm (Table 6). The cubes were stored in water until the 7th day and then in a standard 20/65 climate until testing. The values of 46 MPa to 51 MPa are very close to each other and correspond to concrete strength class C35/45.

Table 6: 28 d-Compressive strength of concrete

Age [d]	Compressive strength [MPa]			
	CCF-2-60	CCF-1-70	CCF-1-75	CCF-2-80
28	51.2	51.1	50.8	46.3

3.4 Frost resistance

The tests for freeze-thaw resistance (CIF method) were carried out in accordance with the BAW data sheet ‘Frost testing of concrete (MFB) [17]. In this test, the internal structural damage is determined using the ultrasonic transit time and the relative dynamic modulus of elasticity derived from this. An additional criterion is the external damage, which is determined by the amount of weathering of the surface.

After the specified 28 days of pre-storage, the samples were pre-stored in demineralised water for 7 days in accordance with the BAW data sheet and then subjected to the freeze-thaw test with 28 freeze-thaw cycles.

The dynamic modulus of elasticity and the dried mass of the weathered components of the concrete were determined at regular intervals.

For each test series, Fig. 2 shows the mean values of the relative modulus of elasticity and Fig. 3 shows the mean values of the determined scaling quantities (cumulative). Fig. 2 shows that the concretes analysed here all comply with the acceptance criterion for the relative modulus of elasticity of 75 % specified in the BAW code of practice. The relative modulus of elasticity values determined were between 83 and 86 %.

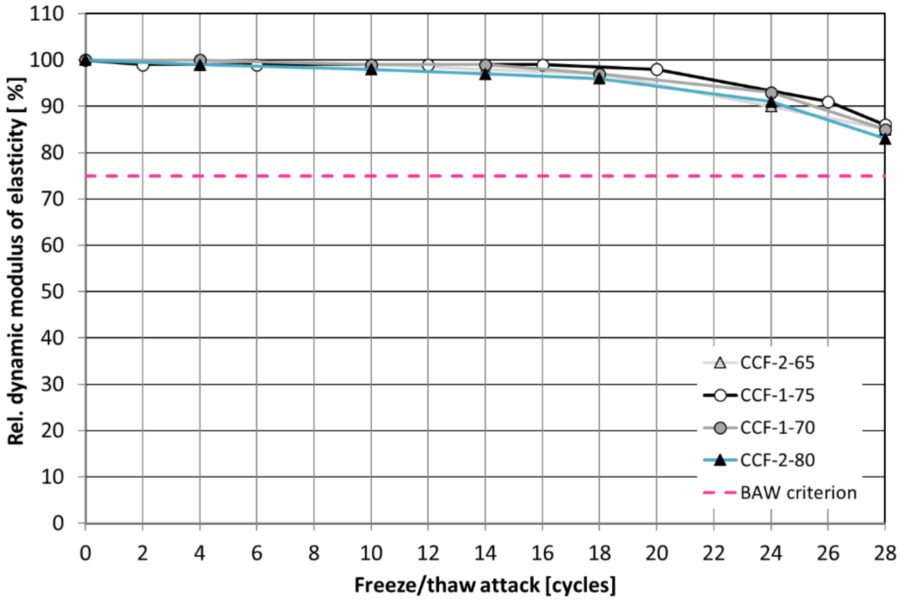

Fig. 2: Relative dynamic modulus of elasticity at CIF-Test

The weathering determined as an additional criterion (Fig. 3) was in a very low range between 25 and 34 g/m². This BAW criterion of 1000 g/m² was also reliably met for all concretes.

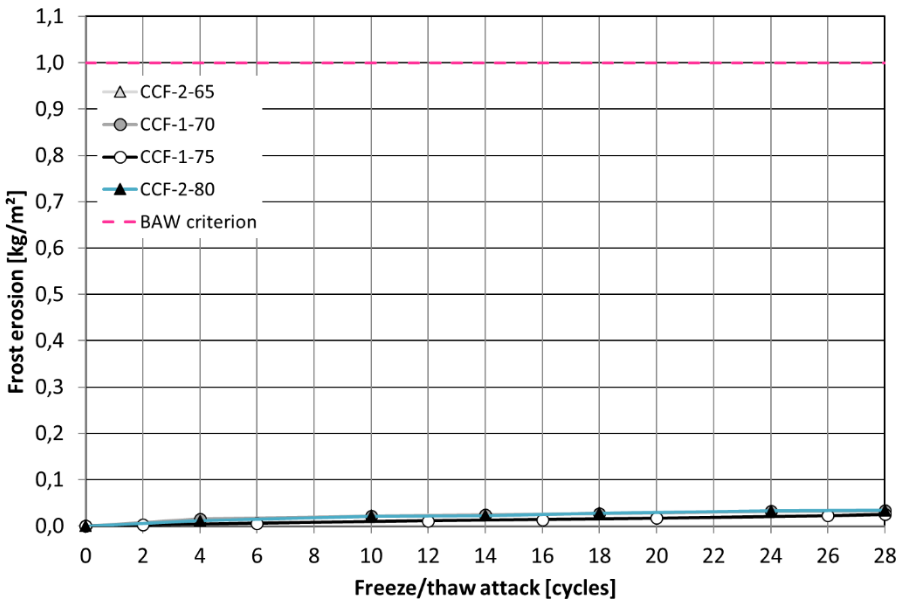

Fig. 3: Defrosting process of concrete at CIF-Test

3.5 Chloride penetration resistance

The resistance of the concrete to penetrating chlorides was tested using a rapid method, the chloride migration test in accordance with the BAW data sheet 'Chloride penetration resistance' (MCL) [18]. The test was carried out after 35 and 97 days on samples stored in water.

A 10 % sodium chloride solution was used as the electrolyte solution for the test. At the end of the test, the so-called migration coefficient DCl was calculated from the penetration depth according to the method specified in the BAW data sheet [18]. After 35 days, the investigations resulted in an average chloride migration coefficient DCl of between 17.2 and 23.1-10^{-12} m²/s. After 97 days, the DCl values were between 13.7 and 21.2-10^{-12} m²/s (Fig. 4). This corresponds to the usual range of 10 to 25-10^{-12} m²/s for Portland cements [19].

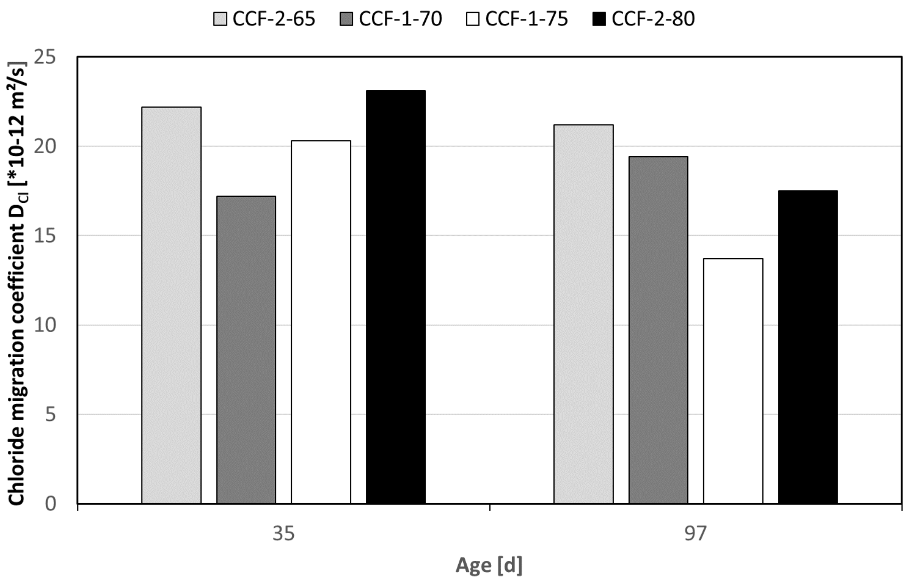

Fig. 4: Defrosting process of concrete at CIF-Test

3.6 Carbonation behaviour

The tests for carbonation behaviour were carried out on fine concrete prisms measuring 40 mm x 40 mm x 160 mm using the current standard procedure for binders in accordance with DIN CEN/TR 16563 [20], Annex B.2. The prisms were pre-stored in water at (20±2)°C for 7 days. The samples were then stored in a climatic chamber at (20±2)°C and (65±5) % RH.

During this storage, also known as main storage, the carbonation depths were determined at regular intervals. To evaluate the carbonation resistance, the carbonation depths after 140 days of main storage are compared with the compressive strength after 7 days of pre-storage. In Fig. 5, these two values are categorised in the evaluation background in accordance with Annex B.7 of DIN CEN/TR 16563 [20]. The results show that the tested binder mixtures were within the permissible range below the limit value function after 7 days of storage.

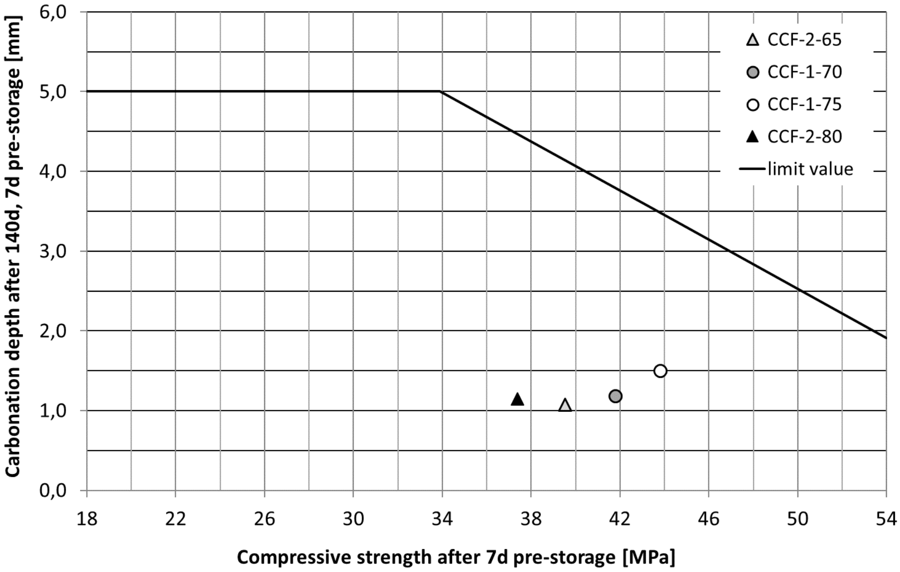

Fig. 5: Classification in the assessment background according to Annex B in [20]

4. SUMMARY

At the Otto Graf Institute of the MPA University of Stuttgart, investigations were carried out into the suitability of limestone filler aggregates with a reduced $CaCO_3$ content for the production of concrete.

The tests showed that the range of $CaCO_3$ content variations tested here exhibited equivalent performance characteristics. The existing regulation in the approvals with regard to the $CaCO_3$ content could therefore be extended. This means that limestones containing dolomite can also be used within the scope of these technical regulations.

The use of the tested limestone filler aggregates in combination with CEM I 42.5 R cement is suitable for all exposure classes except for XF4. If the suitability of this binder combination has been proven in an approval test, the combination of up to 18 % by mass limestone filler aggregates and at least 82 % by mass portland cement CEM I may be used in concrete in accordance with DIN EN 206-1 [6]/ DIN 1045-2 [13] analogous to the existing regulations in Table F.3.1 for the cement type CEM II/A-LL in accordance with DIN EN 197-1 [2].

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