vdz.

C. Müller, S. Palm, Research Institute of the Cement Industry, Duesseldorf,
A. Wolter, T. Bohne, TU Clausthal, Clausthal-Zellenfeld, Germany

SUMMARY

The initial position for the research project was the increase in general technical approvals for cements that according to DIN 1045-2 are not approved in principle in Germany for all exposure classes. Various durability tests that are described in, for example [1], have to be carried out as part of the approval procedure. However, the corresponding test procedures are time-consuming and cost intensive. In a joint research project VDZ gGmbH and Clausthal Technical University have therefore identified some characteristic values based on degree of hydration that allow conclusions to be drawn about durability criteria. This could support and possibly accelerate the procedure for assessing cements that require general technical approval. Before the actual durability testing, which is not to be replaced but only amplified by the results of this research project, it is possible to test whether a cement is suitable to pass such a test. The concrete mix formulations are precisely defined in the approval test plans so the characteristic values developed in this research project are not aimed at concretes with arbitrary compositions but at cements with arbitrary compositions in defined concrete mix formulations. It has been possible to show that in most cases the concrete or mortar compressive strengths of the cements investigated in this research project provided only weak guide values or none at all for the results of the durability investigations. On the basis of the degree of hydration of the hardened cement paste and the porosity of standard mortars it was possible to identify characteristic values that seem suitable for carrying out an assessment with respect to the particular acceptance criteria of the durability tests. No tests on hardened concrete are needed for determining the characteristic values. The durability of concretes with compositions that conform to the approval test plans can be estimated with the aid of the properties of the hardened cement paste and mortar.

ZUSAMMENFASSUNG

Ausgangspunkt des Forschungsvorhabens war die Zunahme von bauaufsichtlichen Anwendungszulassungen für Zemente, die in Deutschland nach DIN 1045-2 nicht prinzipiell für alle Expositionsklassen zugelassen sind. Im Rahmen des Zulassungsverfahrens sind verschiedene Dauerhaftigkeitsprüfungen durchzuführen, die zum Beispiel in [1] beschrieben sind. Die entsprechenden Prüfverfahren sind jedoch zeit- und kostenintensiv. Die VDZ gGmbH und die Technische Universität Clausthal haben deshalb in einem gemeinsamen Forschungsvorhaben Hydratationsgrad basierte Kennwerte ermittelt, die Rückschlüsse auf Dauerhaftigkeitskriterien zulassen. Das Verfahren zur Beurteilung von Zementen, die eine allgemeine bauaufsichtliche Zulassung erfordern, könnte damit unterstützt und ggf. beschleunigt werden. Vor der eigentlichen Dauerhaftigkeitsprüfung, die durch die Ergebnisse dieses Forschungsvorhabens nicht ersetzt, sondern nur ergänzt werden soll, kann festgestellt werden, ob ein Zement geeignet erscheint, eine solche Prüfung zu bestehen. Da in den Zulassungsprüfplänen die Betonrezepturen genau definiert sind, zielen die in diesem Forschungsvorhaben entwickelten Kennwerte nicht auf beliebig zusammengesetzte Betone, sondern auf beliebig zusammengesetzte Zemente in definierten Betonrezepturen ab. Es konnte gezeigt werden, dass die Beton- bzw. Mörteldruckfestigkeit der in diesem Forschungsvorhaben untersuchten Zemente in den meisten Fällen nur schwache bzw. keine Orientierungswerte für die Ergebnisse der Dauerhaftigkeitsuntersuchungen liefert. Auf Basis des Hydratationsgrads von Zementstein sowie der Porosität von Normmörteln konnten Kennwerte ermittelt werden, die geeignet erscheinen, eine Bewertung hinsichtlich des jeweiligen Abnahmekriteriums der Dauerhaftigkeitsprüfungen zu ermöglichen. Für die Bestimmung der Kennwerte sind keine Versuche am Festbeton notwendig. Die Dauerhaftigkeit der zulassungskonform zusammengesetzten Betone lässt sich anhand von Zementstein- und Mörteleigenschaften abschätzen.

(Translation by Robin B. C. Baker)

Characteristic values based on degree of hydration for predicting the durability of concrete

Hydratationsgrad basierte Kennwerte zur Vorhersage der Dauerhaftigkeit von Beton

1 Introduction

If a concrete has the correct composition and has been properly produced and cured its essential characteristics as a construction material are not only its strength but also its durability. If cements are to be used for which there is no practical construction experience then it is necessary to check whether durable concrete can be produced with them. In Germany this requires general technical approval from the DIBt (German Institute for Building Technology). The tests that have to be carried out are laid down in corresponding test plans and assess the suitability of the corresponding cements on the basis of predetermined criteria.

In a joint research project the VDZ gGmbH (German Cement Works Association) and Clausthal Technical University have investigated whether it is possible to determine characteristic values based on the degree of hydration that permit conclusions to be drawn about durability criteria. Before the actual durability testing during the approval procedure it could be possible to test whether a cement seems suitable for passing such a approval procedure. The concrete mix formulations are precisely defined in the approval tests in Germany so the characteristic values developed in this research project are aimed not at concretes with arbitrary compositions but at cements with arbitrary compositions in defined concrete mix formulations. These are listed in ❱ Table 1.

2 Constituents and methods

Two Portland cements and five other main cement constituents (two granulated blastfurnace slags, two fly ashes from bituminous coal and a limestone) with differing finenesses were selected (❱ Fig. 1). 28 laboratory cements, within and outside the limits of the current DIN EN 197-1, were produced from these components. The proportion of clinker, calculated without the secondary constituents and sulfate agent, lay between 50 and 100 mass %. Other main constituents were each used in proportions between 0 and 35 mass %. Cements from approval procedures – after clearance from the submitter – were also included anonymously in the project to extend the data base. Concretes were produced from these cements in accordance with the guidelines from the DIBt approval process (see Table 1) and tested for compressive strength and durability.

The freeze-thaw resistance was tested by the cube method specified in DIN EN 12390-9 and by the CIF method specified by CEN/TR 15177. The resistance to freeze-thaw with de-icing salt was determined by the CDF method specified in DIN EN 12390-9. The chloride penetration resistance (migration coefficient) was tested by the rapid test specified in the code of practice [2] issued by the BAW (Federal Waterways Engineering and Research Institute). The resistance to carbonation was determined on fine concretes with w/c = 0.50 and the A8/B8 grading curve after preliminary storage for 7 or 28 days as described in [1].

3 Evaluation and characteristic values

3.1 General

Not only the progress of hydration but also the pore system that is formed are of crucial importance for the durability of a concrete. During freeze-thaw stressing the air void system also has an influence on the scaling and the damage to the internal microstructure. Appropriate parameters were therefore evaluated for deriving characteristic values for predicting the durability. The degree of hydration (HG) of the hardened cement paste was determined at different test ages. Cement paste samples, in which the hydration was stopped after 2 days, 7 days or 28 days by grinding in acetone, washing with diethyl ether and then vacuum drying, were produced for this purpose. The hardened cement paste samples were then heated to a temperature of 1 250 °C for simultaneous thermal analysis and the loss in mass attributable to water was evaluated with a mass spectrometer in the exhaust gas stream.

The degree of hydration (HG) of the samples was calculated from this mass loss Δm using the equation $HG = \frac{\Delta m}{0.23}$ as described by Locher [3]. The pore size distribution was investigated in the standard mortar at 28 days as specified in DIN 66133. The pore size distribution was evaluated not only with respect to discrete values (❱ Fig. 2) but also by interpolation using two straight lines (❱ Fig. 3). The slopes of the two straight lines S1 and S2 were evaluated as well as the point of intersection of the straight lines (limit radius r_G).

The air content (L) was determined in fresh and hardened concrete but can also be estimated to a first approximation using empirical values. These parameters and parameter

Table 1: Concrete mix formulations and tests

Concrete	Cement content	w/c	Air content in the fresh concrete[1]	Hardened concrete tests
FB[2]	450 g/mixture	0.50	No specification	Compressive strength, carbonation
B2	300 kg/m³	0.60	No specification	Freeze-thaw cube test
B3	320 kg/m³	0.50	No specification	Compressive strength, CIF, chloride migration resistance
B4	320 kg/m³	0.50	(4.5 ± 0.5) %	Compressive strength, CDF

[1] In accordance with DIN EN 12350-7

[2] Fine concrete mix formulation with 1 350 g sand and gravel with the A8/B8 grading curve

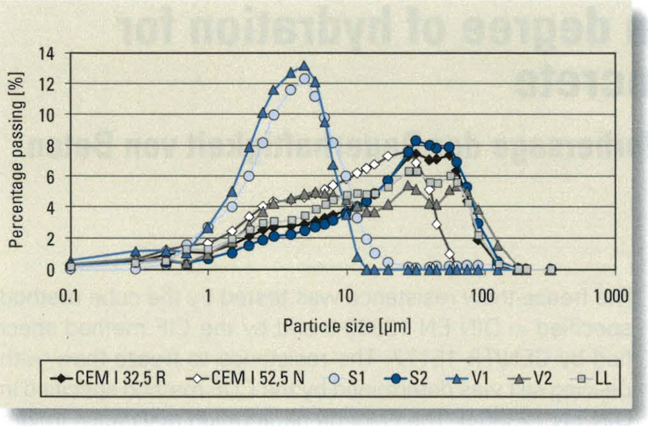

Figure 1: Particle size distributions of the starting materials

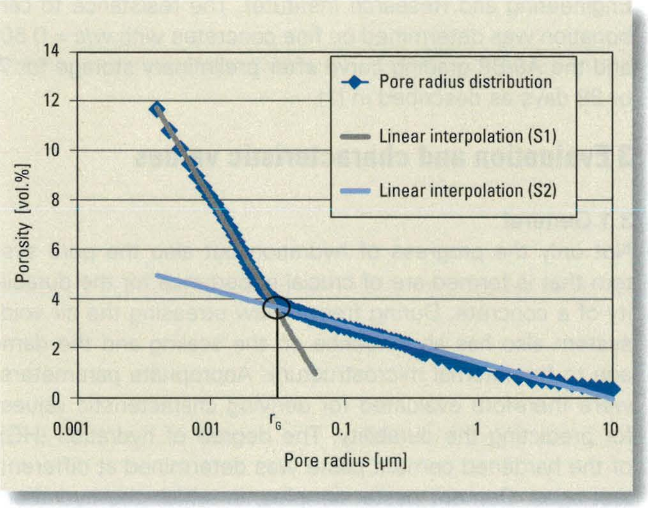

Figure 2: Evaluation of the pore radius distribution using discrete values

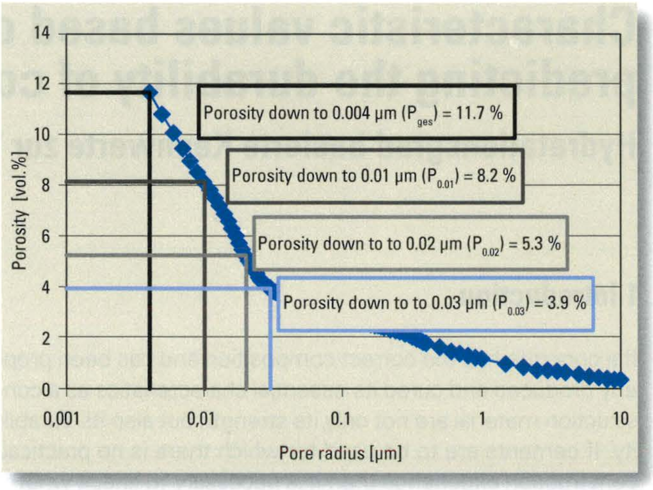

Figure 3: Evaluation of the pore radius distribution by linear interpolation

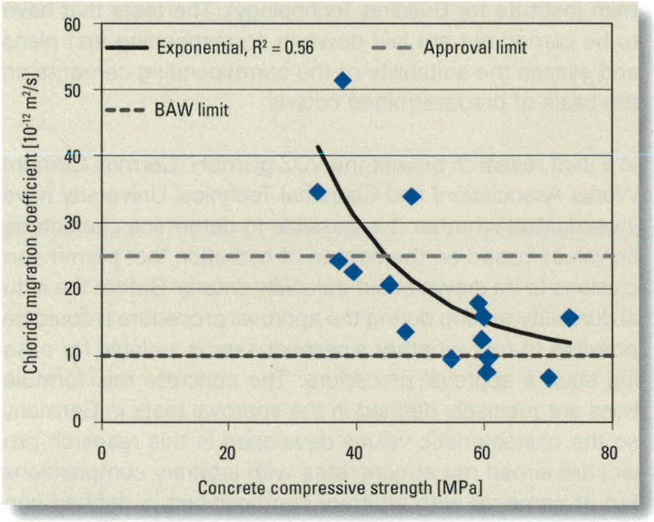

Figure 4: Correlation between the chloride migration coefficients and the concrete compressive strength

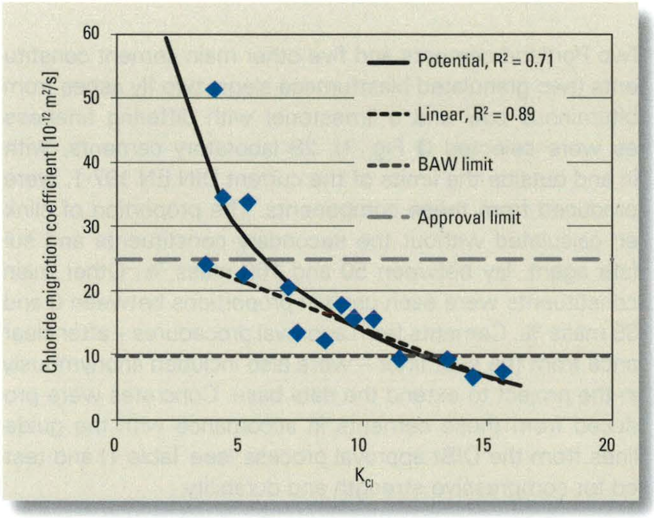

Figure 5: Correlation between the chloride migration coefficients and the characteristic value K_{Cl}

combinations were correlated with the results of the durability investigations at the respective times of evaluation. The following diagrams show the best correlation, in terms of the correlation coefficient R^2, for each case.

3.2 Resistance to chloride migration

The correlations between the chloride migration coefficients of the B3 concrete after 35 days and the concrete compressive strength and a characteristic value (K_{Cl}) are shown in ❯ Fig. 4 and ❯ Fig. 5 respectively.

A limit of $DCl = 25 \times 10^{-12}$ m²/s applies for technical approvals in Germany [1]. In the hydraulic engineering sector a value of $DCl = 10 \times 10^{-12}$ m²/s applies for exposure classes XD1, XD2, XS1 and XS2 in accordance with the BAW code of practice "Chloride penetration resistance" [2].

Fig. 4 shows that in principle there is a relationship between concrete compressive strength and chloride penetration resistance. However, no reliable information concerning the above-mentioned limits can be obtained from this relationship.

The relationship between the characteristic value $K_{Cl} = HG \frac{HG_{7d}}{P_{0.02}}$ and the chloride penetration resistance is shown in Fig. 5. The correlation coefficient of $R^2 = 0.71$ is significantly larger. For a cement that requires building inspectorate application approval and has a characteristic value of at least $K_{Cl} > 7$ it can be assumed that the chloride penetration resistance test will be passed. For the hydraulic engineering sector the characteristic value would have to be $K_{Cl} > 12$.

3.3 Freeze-thaw resistance (cube method)

The correlations between freeze-thaw resistance (cube method) of the B2 concrete and the concrete compressive strength and a characteristic value $K_{WF} = -1 \times HG_{2d} \times L \times \frac{S2}{r_G}$ are shown in ❯ Fig. 6 and ❯ Fig. 7 respectively.

A maximum scaling of 10 mass % after 100 freeze-thaw cycles is the limit in the approval procedure in Germany [1].

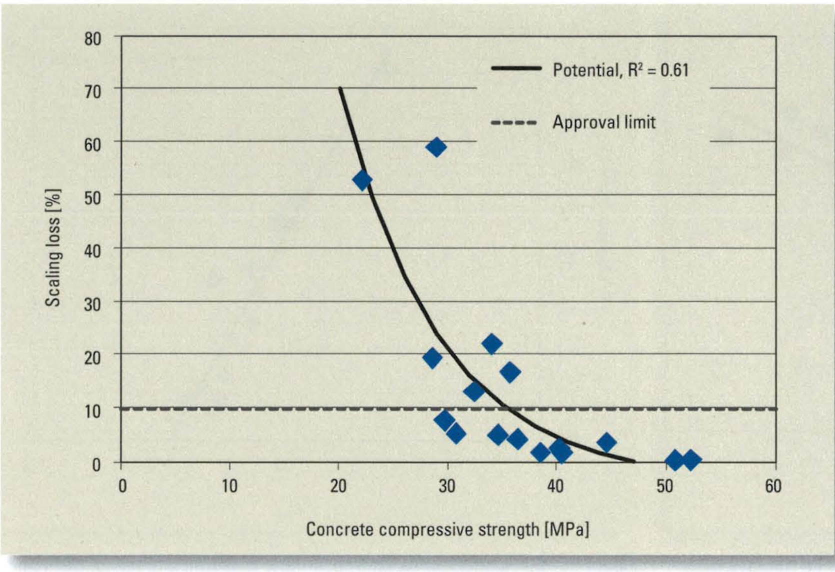

Figure 6: Correlation between freeze-thaw resistance (cube test) and concrete compressive strength

Fig. 6 shows a relationship in principle between the concrete compressive strength and the scaling. Above a strength of ≥ 40 MPa it can be assumed that the freeze-thaw resistance test by the cube method will be passed. However, the relationship shows a certain lack of clarity in the range between 30 and 40 MPa.

The correlation coefficient between the characteristic value KWF and the scaling by the cube method is R^2 = 0.9. For a cement that requires building inspectorate application approval and has a characteristic value of at least KWF > 500 it can be assumed that the test of freeze-thaw resistance by the cube method will be passed.

3.4 Freeze-thaw resistance (CIF method)

The correlations between the freeze-thaw resistance by the CIF method of the B3 concrete and the concrete compressive strength and a characteristic value $K_{CIF,E}$ (for the relative dynamic modulus of elasticity) are shown in ❱ Fig. 8 and ❱ Fig. 9 respectively.

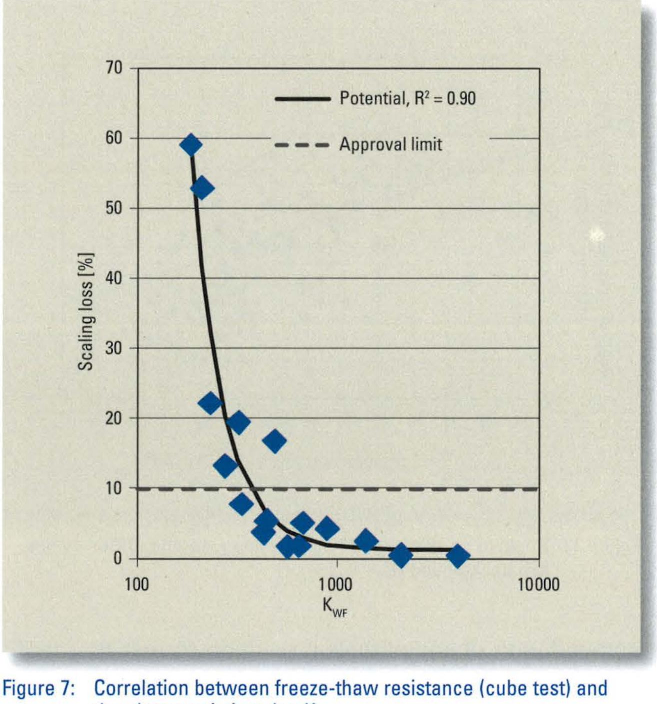

Figure 7: Correlation between freeze-thaw resistance (cube test) and the characteristic value K_{WF}

According to [4], it is to be expected that a concrete that does not have the correct composition will essentially suffer internal damage to the microstructure during freeze-thaw attack by the CIF method. A relative dynamic modulus of elasticity of at least 75 % after 28 freeze-thaw cycles is therefore the essential acceptance criterion in Germany in some application sectors [1, 5]. Maximum scaling of 1.0 kg/m² is an additional acceptance criterion.

In Fig. 8 it is clear that the concrete compressive strength is not sufficient to provide reliable prediction of the "relative dynamic modulus of elasticity" acceptance criterion. In particular, concretes with a concrete compressive strength of about 50 to 60 MPa can exhibit significant differences in relative dynamic modulus of elasticity after 28 freeze-thaw cycles. The values here lie between 97 and 59 % and therefore fluctuate around the acceptance criterion.

The relationship between the characteristic value $K_{CIF,E} = \frac{HG_{28d}}{P_{0.02}}$ and the relative dynamic modulus of elasticity is shown in Fig. 9. This relationship is linear. Above a characteristic value of about 14 the acceptance criterion are safely satisfied by the cements and concretes used in the research project.

3.5 Resistance to freeze-thaw with de-icing salt (CDF method)

The correlations between scaling of the B4 concrete after 28 freeze-thaw cycles in the CDF method and the concrete compressive strength and a characteristic value (KCDF) are shown in ❱ Fig. 10 and ❱ Fig. 11 respectively.

It is to be expected that freeze-thaw attack with de-icing salt in the CDF method will mainly result in damage to the surface (scaling). The acceptance criterion in Germany is therefore usually a maximum scaling of 1.5 kg/m² after 28 freeze-thaw cycles [1, 5]. A relative dynamic modulus of elasticity of at least 75 % after 28 freeze-thaw cycles is an additional acceptance criterion [5]. This was satisfied by all the concretes investigated.

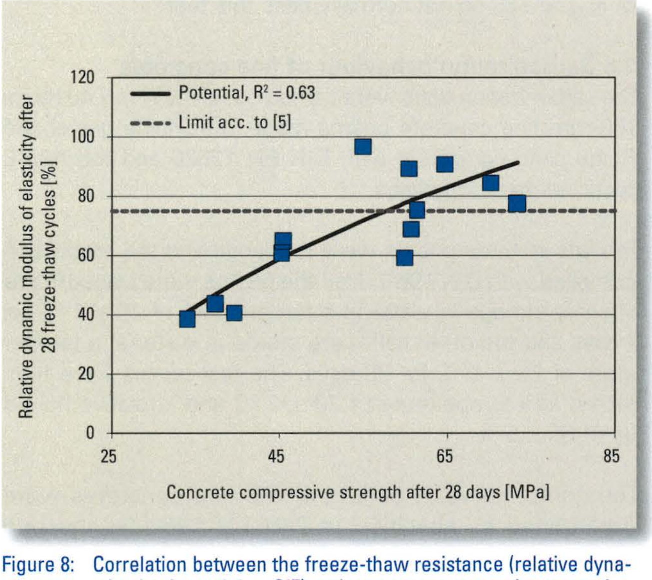

Figure 8: Correlation between the freeze-thaw resistance (relative dynamic elastic modulus, CIF) and concrete compressive strength

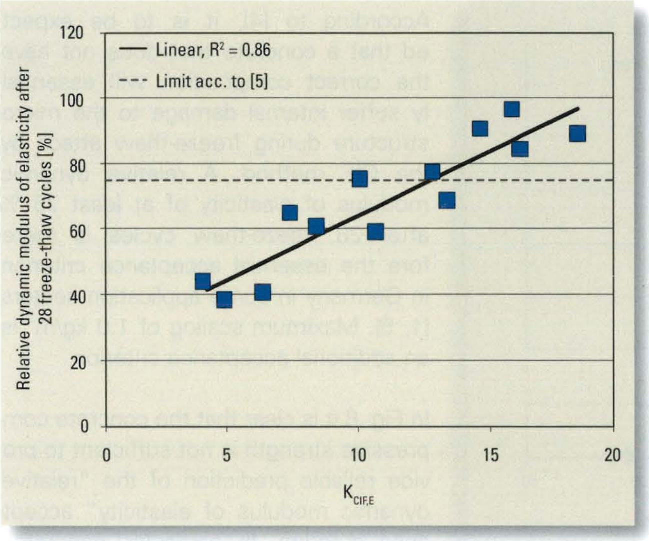

Figure 9: Correlation between the freeze-thaw resistance (relative dynamic elastic modulus, CIF) and the parameter $K_{CIF,E}$

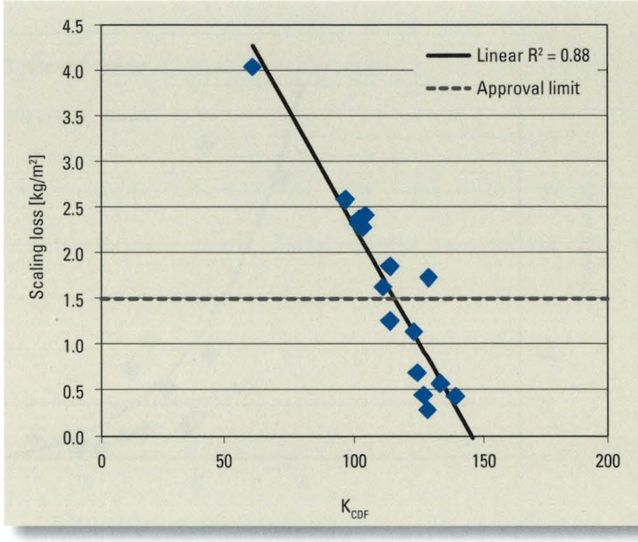

Figure 11: Correlation between freeze-thaw resistance (scaling, CDF) and the characteristic value K_{CDF}

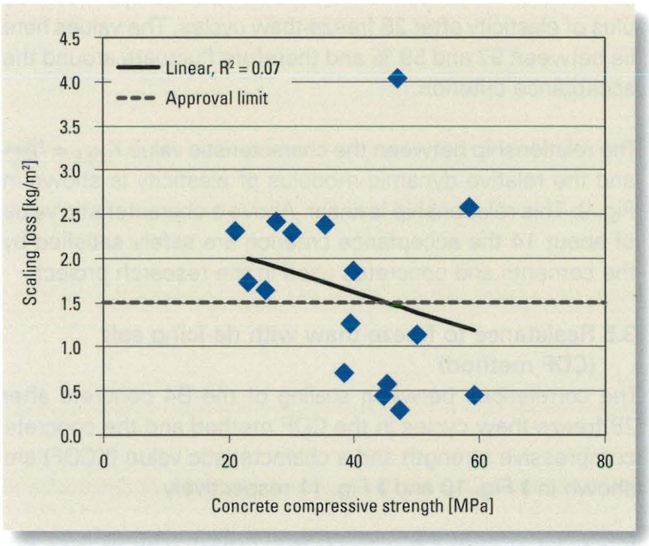

Figure 10: Correlation between freeze-thaw resistance (scaling, CDF) and concrete compressive strength

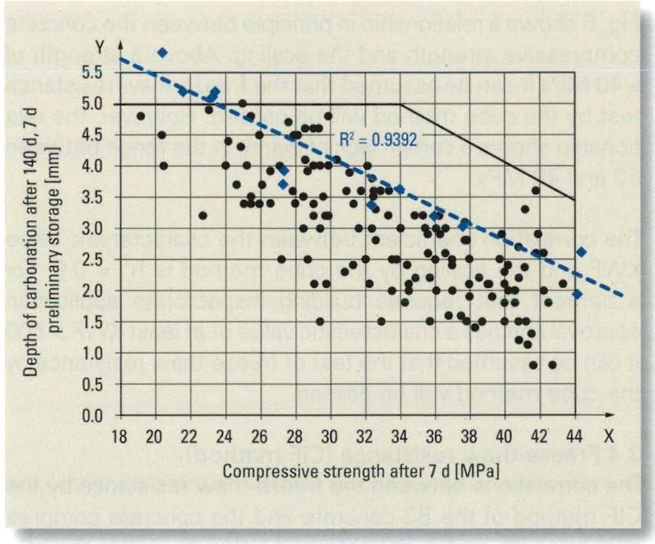

Figure 12: Depth of carbonation, 7 d preliminary storage, DIBt's evaluation background [1]

There is no relationship between concrete compressive strength and the scaling (Fig. 10). Fig. 11 shows the linear correlation of the scaling with the characteristic value $K_{CDF} = HG_{2d} \times L \times \frac{P_{0.01}}{P_{ges}}$. Cements with a characteristic value of $K_{CDF} < 120$ do not normally pass this test.

3.6 Carbonization behaviour of fine concretes

The carbonization tests were carried out on 40 mm x 40 mm x 160 mm fine concrete prisms made with Rhine gravel and Rhine sand complying with DIN EN 12620 and the A8/B8 particle size composition.

Ten lots of three prisms were produced and the production complied with DIN 196-1. Half the prisms were placed in preliminary storage in water at a temperature of 20 ± 1 °C for 7 days and the other half were stored in water at a temperature of 20 ± 1 °C for 28 days. The test pieces were then stored at a temperature of 20 ± 2 °C and a relative humidity of 65 ± 5 %.

The compressive strengths of the fine concretes were determined as specified in DIN EN 196-1 at the end of the preliminary storage (7 or 28 days). Pieces about 30 mm long were split from each of three test pieces and

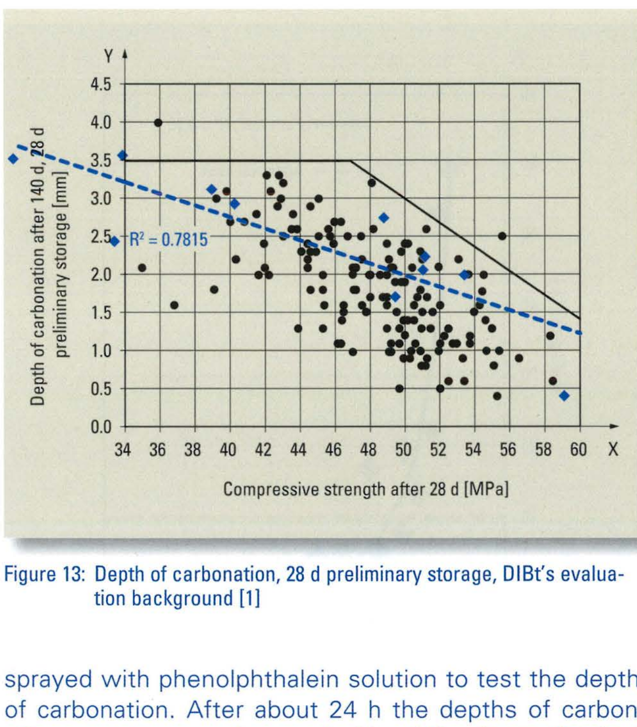

Figure 13: Depth of carbonation, 28 d preliminary storage, DIBt's evaluation background [1]

sprayed with phenolphthalein solution to test the depth of carbonation. After about 24 h the depths of carbonation were measured on each side of the pieces that had been split off and the average depth of carbonation was calculated. The corner regions were not taken into account. The test dates were set at 14 days, 56 days, 98 days, 140 days and one year of main storage. Most of the measured values lay well below the level specified by the DIBt [1]. No attempt was made to determine characteristic values based on degree of hydration and pore radius distribution.

4 Summary

It has been possible to show that in most cases the concrete or mortar strengths of the cements investigated in this research project provide only weak guide values or none at all for the results of the durability investigations. On the basis of the degree of hydration of the hardened cement paste and the porosity of standard mortars it was possible to identify characteristic values that seem suitable for carrying out an assessment with respect to the particular acceptance criteria of the durability tests. No tests on hardened concrete are needed for determining the characteristic values. The durability of concretes with compositions that conform to the approval test plans can be estimated with the aid of the properties of the hardened cement paste and mortar.

A limited number of cements and main cement constituents were used in the research project. Further investigations must be carried out to confirm the results.

Acknowledgement

The IGF project 17123 N was sponsored by the Federal Ministry of Economics and Energy through the AiF (Federation of Industrial Cooperative Research Associations) as part of the programme to promote Joint Industrial Research (IGF) based on a decision by the Germany Federal Parliament.

LITERATURE

[1] Principles of the equivalent durability procedure. CEN/TR 16563, 2013.
[2] Chlorideindringwiderstand von Beton. Merkblatt der Bundesanstalt für Wasserbau (BAW), Karlsruhe 2004.
[3] Locher, F. W.: Zement: Grundlagen der Herstellung und Verwendung. Verlag Bau und Technik, Düsseldorf 2000.
[4] Setzer, M. J.: Frostschaden: Grundlagen und Prüfung. Beton und Stahlbetonbau 97 (2002) H. 7, pp. 350–359.
[5] Frostprüfung von Beton. Merkblatt der Bundesanstalt für Wasserbau (BAW), Karlsruhe 2004.