Dr. C. Müller, Dipl.-Ing. K. Severins, Research Institute of the Cement Industry, Düsseldorf, Germany

SUMMARY

On the basis of the results of research work at the technical universities in Aachen and Munich [1] Appendix A2 to DIN 1045-2 will in future allow to use the k-value concept for coal fly ash as a concrete addition in concrete exposed to freeze-thaw attack with de-icing salt (exposure classes XF2 and XF4). This also means that cements that contain fly ash are no longer excluded from use. If fly ash is used as a main constituent in Portland-composite cements then in some cases partly higher levels of fly ash can be employed than if it is used as a concrete addition because a practical performance level can be established in the concrete through the use of optimized cements. In the context of research funded by the AiF, investigations were carried out at the Research Institute of the Cement Industry that focused on freeze-thaw tests with and without de-icing salt because of the restrictions to the use of cements containing fly ash that applied up to the publication of the A2 amendment to DIN 1045-2. The carbonation behaviour and the resistance to chloride penetration of the concretes were also examined. The aim of the investigations was to compile an extended database for concretes made using Portland-composite cements containing fly ash. This research project [3] follows on from investigations into the durability of concrete made with Portland-limestone cements and Portland-composite cements CEM II-M (S-LL) that were discussed in detail in CEMENT INTERNATIONAL 4 (2006) No. 2, pp. 120-125. The production and processing of the cements and concretes as well as the test methods used are modelled on these investigations.

ZUSAMMENFASSUNG

Auf der Basis der Ergebnisse einer Forschungsarbeit an den Technischen Universitäten in Aachen und München [1] wird zukünftig mit der Ergänzung A2 zur DIN 1045-2 die Anrechnung von Steinkohlenflugasche als Betonzusatzstoff in Beton bei Frost-Tausalz-Angriff (Expositionsklassen XF2 und XF4) erlaubt. Somit wird auch die Anwendung flugaschehaltiger Zemente nicht mehr ausgeschlossen. Wird Flugasche als Hauptbestandteil in Portlandkompositzementen eingesetzt, können z.T. höhere Flugaschegehalte als in der Verwendung als Betonzusatzstoff realisiert werden, da durch die Verwendung optimierter Zemente ein praxisgerechtes Leistungsniveau im Beton eingestellt wird. Im Rahmen der AiF-Forschungsförderung wurden Untersuchungen im Forschungsinstitut der Zementindustrie durchgeführt, die wegen der bis zur Veröffentlichung der A2-Änderung zu DIN 1045-2 geltenden Anwendungsbeschränkungen für flugaschehaltige Zemente schwerpunktmäßig Frost- und Frost-Tausalz-Versuche beinhalteten. Ergänzend wurden aber z.B. auch das Carbonatisierungsverhalten und der Chlorideindringwiderstand der Betone untersucht. Ziel der Untersuchungen war es, eine erweiterte Datengrundlage für Betone unter Verwendung flugaschehaltiger Portlandkompositzemente zu erarbeiten. Dieses Forschungsvorhaben [3] schließt an Untersuchungen zur Dauerhaftigkeit von Beton mit Portlandkalksteinzementen und Portlandkompositzementen CEM II-M (S-LL) an, die in CEMENT INTERNATIONAL 4 (2006) Nr. 2, S. 120-125, ausführlich dargestellt wurden. Die Herstellung und Verarbeitung der Zemente und Betone sowie die verwendeten Prüfverfahren lehnen sich an diese Untersuchungen an.

Durability of concretes made with cements containing fly ash

Dauerhaftigkeit von Betonen mit flugaschehaltigen Zementen

1 Introduction

The use of cements with several main constituents raises the eco-efficiency of concrete construction. Through the reduction of the clinker content these cements provide a means of limiting the CO_2 emissions per tonne of cement during the production of cement. Cements with several main constituents also have the advantage that, due to the greater range of available cements, the properties of the concrete can be better adapted to suit the particular application.

The appendix to DIN 1045-2 allows to use the k-value concept for coal fly ash as a concrete addition in concrete exposed to freeze-thaw attack with de-icing salt (exposure classes XF2 and XF4). This also means that cements that contain fly ash are no longer excluded from use. Until recently there had been few systematic investigations in Germany into the influence of cements that contained fly ash on the resistance of concrete to freeze-thaw with and without de-icing salt – taking particular account of the requirements for the concrete composition for concretes exposed to freeze-thaw or to freeze-thaw with de-icing salt laid down in the DIN Technical Report 100 "Concrete" [4].

The aim of the research project was therefore to compile a comprehensive database for concretes made with cements containing fly ash. The investigations concentrated on the durability of the concretes, especially their resistance to freeze-thaw with and without de-icing salt. They also dealt with the use of the k-value concept for fly ash as a concrete addition when using cements containing fly ash. However, no freeze-thaw trials with de-icing salt were carried out with fly ash as a concrete addition as investigations into this topic formed part of a research programme that was carried out at the Munich Technical University and the Aachen University of Technology [1].

2 Test programme

2.1 Constituents

The test cements were composed of the main constituents, namely clinker (K), granulated blastfurnace slag (S), limestone (LL with TOC ≤ 0.20 wt. %) and coal fly ash (V1, V2 and V3), and an optimized mixture of sulfate agents.

The fly ash (› Table 1) came from two different power stations; fly ashes V1 and V3 were of the same origin. The fly ashes exhibited some differences, especially in their fineness and loss on ignition, and also varied in the levels of Al_2O_3, Fe_2O_3, CaO and SiO_2. All the fly ashes investigated here complied with DIN EN 450-1 and DIN EN 197-1. According to DIN EN 197-1 fly ash V1 is only allowed to be used under certain preconditions because of its high loss on ignition of 6.96 wt. %. These preconditions include requirements for durability and compatibility with admixtures in accordance with the instructions applying at the place of use, but also the designation of the loss on ignition on the packaging and the delivery document.

In addition to the use of fly ashes V1, V2 and V3 as main cement constituents fly ash V2 was also used as an addition in the concrete and included in the calculation of the equivalent water/cement ratio with a k value of 0.4.

Aggregates (Rhine sand and gravel, from the stock at the research establishment) with the A16/B16 particle size composition as defined in DIN 1045-2, Appendix L, were used for producing the concretes. The coarse aggregates fulfilled the requirements for aggregates for exposure classes XF3 and XF4 as specified in DIN 1045-2 in conjunction with DIN V 20000-103.

2.2 Cement production

Comparative durability investigations carried out on concretes presuppose that the concretes under investigation have a comparable strength level as a characteristic indicating a similar formation of the microstructure. It was therefore intended that the cements under investigation should have comparable 28 day strengths, which in the relevant range of German cements of the 32,5 R strength class lie between about 44 MPa and 48 MPa. The particle size distributions of the main cement constituents, namely Portland cement clinker, coal fly ash, granulated blastfurnace slag and limestone, therefore had to be varied so that the specified strength level was approximately achieved by the different cement compositions.

The granulometry of the cements containing fly ash that were produced in the laboratory was optimized. The clinker, granulated blastfurnace slag and limestone were ground in semi-industrial laboratory ball mills and then mixed with the fly ash (predominantly in its original state) and with a sulfate agent that had been matched to the required cement mix.

The levels of fly ash lay between 20 wt. % and 35 wt. % in the Portland-fly ash cements, while the Portland-composite cements consisted of 15 wt. % or 25 wt. % fly ash and 10 wt. %,

Table 1: Fly ash properties

Property	Unit	V 1	V 2	V 3
Specific surface area (Blaine)	cm²/g	4700	3700	3350
Loss on ignition	wt.%	6.96	2.88	3.36
Free CaO	wt.%	0.60	0.60	0.50
Chloride	wt.%	0.004	0.004	0.002
Reactive silica	wt.%	35.3	37.7	38.9
Reactive CaO	wt.%	3.95	3.17	3.45
Residue on 0.04 mm (sieving/air jet)	wt.%	13/13	25/25	29/29
Apparent particle density	g/cm³	2.23	2.24	2.20

CONCRETE TECHNOLOGY REPORTS

15 wt. % or 20 wt. % granulated blastfurnace slag and 15 wt. % limestone. A total of eleven cements containing fly ash were produced (❱ Table 2). The coal fly ash V2 that was predominantly used in these cements had a fineness of about 3 700 cm^2/g Blaine. A narrower particle size distribution of the clinker was chosen for the higher fly ash content (35 wt. %) or when using the coarser fly ash V3 in order to achieve a realistic cement strength.

A CEM I 32,5 R cement produced in the factory and a CEM III/A 32,5 R laboratory cement containing 50 wt. % granulated blastfurnace slag were used as reference cements.

2.3 Concrete production

Concretes of varying composition were produced and tested. ❱ Table 3 provides a general summary. The mix compositions of the concretes were directed towards the limit values for the composition and properties of concretes as described in DIN Technical Report 100 "Concrete" [4]. This resulted in five characteristic concrete mix formulations for the concrete trials without the inclusion of fly ash as a concrete addition (B1 to B5). There were also test series that investigated the effects of including fly ash in the calculation of the minimum cement content and the equivalent water/cement ratio when using cements containing fly ash. These concretes were designated B1* to B5*.

Table 3 also provides a summary of all the tests carried out on fresh and hardened concrete. The test methods are not described in detail here. All the tests corresponded to those of the research work into the durability of concretes made with cements containing limestone [2].

3 Description and discussion of the results

3.1 Cement properties

Numerous cements containing 20 wt. % to 35 wt. % fly ash, cements containing ground fly ash and cements containing different fly ashes were produced, granulometrically optimized and tested during the preliminary investigations in order to determine the influence of the content, fineness and quality (loss on ignition) of the fly ash on the cement properties. The effects of fly ash in combination with granulated blastfurnace slag or limestone on the properties of Portland-composite cements were also examined. In some cases the necessary cement properties, such as the required 28 day compressive strength, could not be achieved directly. In isolated cases the cements exhibited comparatively low strength values that lay below the desired value range of 44 MPa to 48 MPa. The test cements were selected on the basis of these results.

The important properties of the cements used in the concrete investigations are listed in Table 2. The 28 day compressive strengths of these test cements achieved values between 39 MPa and 48 MPa. The water demand to achieve standard stiffness varied from 24 wt. % to 33 wt. % depending on the particle size distribution and the composition of the cements.

3.2 Porosity and pore size distribution

The porosity and pore size distribution are of fundamental importance for the properties of cement-bound building materials that are relevant to durability because as a rule any harmful effects find their way into the building material via

Table 2: Compositions and properties of the test cements

Cement		Clinker	Coal fly ash V 1	Coal fly ash V 2	Coal fly ash V 3	Granulated blastfurnace slag	Limestone	Fineness (Blaine)	RRSB slope	Water demand	Compressive strength 2 d	Compressive strength 7 d	Compressive strength 28 d
		Proportions of main constituents in wt.% and Blaine fineness						cm^2/g		wt.%	MPa		
1[1)]	CEM I	100	–	–	–	–	–	2 780	0.77	25.0	20.5	37.5	47.9
2[2)]	CEM II 35 % V2	65 4 080 cm^2/g	–	35 3 700 cm^2/g	–	–	–	4 280	0.94	31.0	23.3	32.3	45.3
3[3)]	CEM II 30 % V2	70 4 500 cm^2/g	–	30[3)] 3 700 cm^2/g	–	–	–	4 530	0.76	26.0	18.2	27.1	39.1
4	CEM II 25 % V2	75 4 000 cm^2/g	–	25 3 700 cm^2/g	–	–	–	4 050	0.74	25.0	20.4	30.2	41.8
5	CEM II 20 % V2	80 4 000 cm^2/g	–	20 3 700 cm^2/g	–	–	–	4 175	0.76	25.0	20.8	32.6	44.4
6	CEM II 30 % V1	70 4 500 cm^2/g	30 4 700 cm^2/g	–	–	–	–	4 715	0.81	30.0	19.1	29.6	41.3
7[2)]	CEM II 30 % V3	70 4 080 cm^2/g	–	–	30 3 350 cm^2/g	–	–	4 220	0.94	33.0	26.2	36.7	48.2
8	CEM II 25 %V2 10 %S	65 4 700 cm^2/g	–	25 3 700 cm^2/g	–	10 3 100 cm^2/g	–	4 410	0.77	26.0	18.2	27.9	42.5
9	CEM II 15 %V2 20 %S	65 4 500 cm^2/g	–	15 3 700 cm^2/g	–	20 3 100 cm^2/g	–	4 315	0.77	24.0	17.9	28.9	44.7
10	CEM II 15 %V2 15 %S	70 4 500 cm^2/g	–	15 3 700 cm^2/g	–	15 3 100 cm^2/g	–	4 355	0.77	25.2	19.4	29.8	45.7
11	CEM II 15 %V2 15 %LL	70 4 300 cm^2/g	–	15 3 700 cm^2/g	–	–	15 7 000 cm^2/g	4 670	0.77	26.0	22.6	33.9	44.4
12	CEM II 30 %V2-4 400	70 4 500 cm^2/g	–	30 4 400 cm^2/g	–	–	–	4 510	0.72	26.5	18.5	28.3	43.2
13	CEM III/A	50 4 500 cm^2/g	–	–	–	50 3 300 cm^2/g	–	4 200	0.75	26.0	13.2	27.3	47.6

1) Commercial CEM I 32.5 R cement with RRSB slope n = 0.8
2) For these cements the clinker meal was produced with a different grinding system in order to achieve a greater RRSB slope of the particle size distribution (n = 1) and hence higher strengths
3) An additional test series was carried out for this composition using fly ashes ground to different finenesses (see Cement 12)

Table 3: Summary of the concrete compositions and test methods

Concrete	c	f	$(w/c)_{eq}$	w/(c+f)	f/(c+f)	AC	FCP	f_{cm}		d_c	CM/CIF	CDF	AVV	D_{Cl}
	kg/m³	kg/m³				Vol. %		2d to 90d	28d					
B1	320	–	0.50	0.50	0	–	x	x	x	–	CIF	–	–	x
B2	300	–	0.60	0.60	0	–	x	–	x	–	CM	–	–	–
B3	300	–	0.55	0.55	0	4.5 to 5.5	x	–	x	–	CIF	–	x	–
B4	320	–	0.50	0.50	0	4.5 to 5.5	x	–	x	–	–	x	x	–
B5	260	–	0.65	0.65	0	–	x	–	x	x	–	–	–	–
B1*	270	89.1	0.50	0.43	0.25	–	x	x	x	–	CIF	–	–	x
B2*	270	89.1	0.60	0.51	0.25	–	x	–	x	–	CM	–	–	–
B3*	270	89.1	0.55	0.47	0.25	4.5 to 5.5	x	–	x	–	CIF	–	x	–
B5*	240	79.2	0.65	0.55	0.25	–	x	–	x	x	–	–	–	–

c: Cement content
$(w/c)_{eq}$: Equivalent water/cement ratio w/(c+0.4·f)
AC: Target air content for the fresh concrete
FCP: Fresh concrete properties
$f_{cm, 2d-90d}$: Concrete compressive strength at 2, 7 and 90 d
$f_{cm, 28d}$: Concrete compressive strength at 28 d
d_c: Depth of carbonation
CM: Freeze-thaw cycle test by the cube method with water
CIF: Freeze-thaw cycle test by the CIF method (with water)
CDF: Freeze-thaw cycle test by the CDF method (with de-icing agent (NaCl))
AVV: Characteristic air void values in the hardened concrete
D_{Cl}: Chloride migration coefficient from the accelerated test
X: Tested
-: Not tested

the pore system. The use of coal fly ash as a main cement constituent can have a crucial influence on the porosity and hence on the durability of a concrete. The pore size distribution of all standard cement mortars (w/c = 0.50, c = 450 g) was measured at 28 days by mercury intrusion porosimetry.

By way of example ❱ Fig. 1 shows the relative porosity after 28 days of the mortars made with cements containing 20 wt. % to 35 wt. % fly ash and with CEM III/A cement compared with the mortar made with the CEM I reference cement. It can be seen from the diagram that the mortars made with cements containing fly ash have a somewhat higher total relative porosity than the mortars made with the CEM I and CEM III/A reference cements. When using cements containing fly ash the proportion of coarser pores > 0.1 µm at 28 days differed only slightly from that with the Portland cement. On the other hand, the increase in the proportion of finer pores < 0.01 µm typical of mortars and concretes containing fly ash was apparent even at this age.

3.3 Concrete compressive strength

❱ Fig. 2 shows an example of the development of the compressive strength of concrete B1 (without addition) with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m³ made with the CEM I and CEM III/A reference cements and with the Portland-fly ash cements containing between 20 wt. % and 35 wt. % fly ash. As a consequence of the granulometric optimization of the cements the strength development of the concretes was analogous to the development of the cement standard compressive strength. As expected, the early strengths of the concretes made with Portland-fly ash cements and with the CEM III/A cement used here were lower than those of the Portland cement concrete. After 28 days the strength values of the concretes lay relatively close to one another.

3.4 Carbonation

Carbonation is crucial for the durability of reinforced concrete. The rate of carbonation is determined by the diffusion of CO_2 through the pore system of the concrete. The depth of carbonation was measured on 100 mm x 100 mm x 500 mm concrete beams using the test method specified in [5].

❱ Fig. 3 shows an example of the development with time of the depths of carbonation of some of the concretes under investigation that had been produced with the two reference

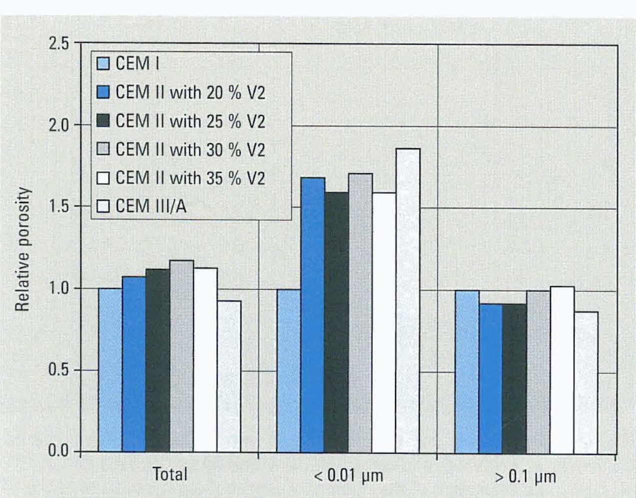

Figure 1: Relative porosity of cement mortars made with Portland-fly ash cements and Portland-slag cement compared to the porosity of CEM I mortar with w/c = 0.50 at 28 days

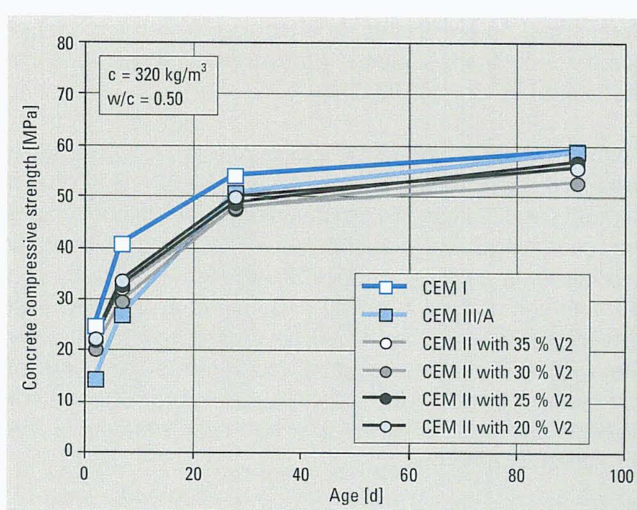

Figure 2: Compressive strengths of concretes (B1) made with Portland-fly ash cements and reference cements as a function of test age and cement composition

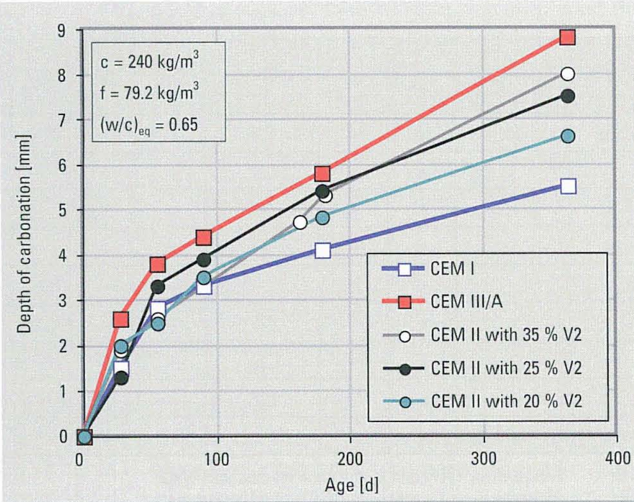

Figure 3: Depths of carbonation of concretes (B5*) made with Portland-fly ash cements and reference cements and fly ash as an addition as a function of test age and cement composition

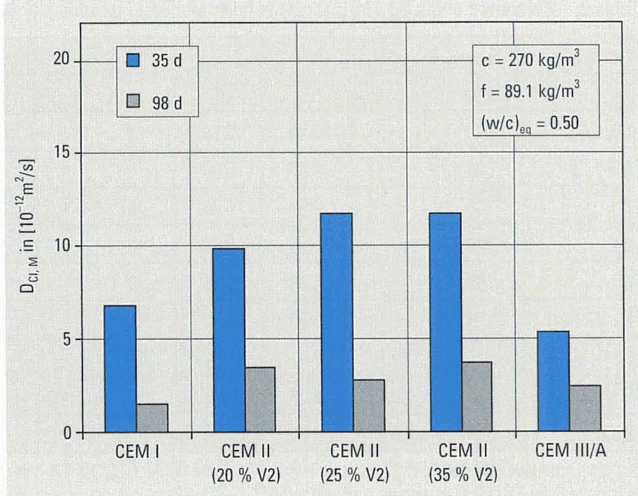

Figure 4: Chloride migration coefficients of concretes (B1*) made with Portland-fly ash cements and reference cements and fly ash as an addition as a function of test age and cement composition

cements and with the Portland-fly ash cements. In this case cements containing fly ash were used in combination with fly ash as an addition. The concretes were produced with a cement content of c = 240 kg/m^3, an equivalent water/cement ratio of $(w/c)_{eq}$ = 0.65 and a fly ash content of f = 79.2 kg/m^3 (f/c = 0.33). The depths of carbonation of the concretes made with cements containing fly ash were less than the values of the CEM III/A concrete. CEM III/A cement can also be used in combination with fly ash as a concrete addition for all application areas (exposure classes). The depths of carbonation of these concretes also lay in the value range that, according to the information in the literature [6, 7], can be assumed for cements CEM I to CEM III/B under the test conditions used here.

The results confirm that these Portland-fly ash cements can be used in all exposure classes for carbonation-induced reinforcement corrosion, including in combination with coal fly ash as a concrete addition. The standard DIN 1045-2 provides additional security when cements containing fly ash are used together with fly ash as a concrete addition by limiting the allowance factor for the fly ash content to f/c = 0.25 instead of the maximum value of f/c = 0.33 that would otherwise apply.

3.5 Resistance to penetration by chlorides

The resistance of the concrete to penetrating chlorides was determined here with the aid of an accelerated test (migration test [8]). The test pieces were stored in water up to the test age of 35 days or 98 days.

Concretes conforming to the exposure class XD2/XS2 were produced with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m^3 (without addition). The chloride migration coefficients $D_{Cl,M}$ determined when using Portland-fly ash cements containing up to 35 wt. % siliceous fly ash lay between about 10 and 20 · 10^{-12} m^2/s at 35 days. Test pieces that were tested at 98 days exhibited significantly reduced $D_{Cl,M}$ chloride migration coefficients that were of the order of 5 to 6 · 10^{-12} m^2/s. The values measured here lie within the range of values specified in the literature [9, 10] for Portland cements.

When Portland-fly ash cements containing 20 wt. %, 25 wt. % and 35 wt. % fly ash as a main cement constituent were used with the simultaneous use of fly ash as a concrete addition these concretes exhibited a chloride migration coefficient $D_{Cl,M}$ after 35 days of between about 10 and 20 · 10^{-12} m^2/s (▸ Fig. 4). After 98 days the values lay at the same level as the CEM III/A concrete made with fly ash ($D_{Cl,M}$ about 3 · 10^{-12} m^2/s).

The results confirm that Portland-fly ash cements combined with coal fly ash as a concrete addition can also be used in all exposure classes for chloride-induced reinforcement corrosion. Here again the concrete standard limits the allowance factor for the fly ash content during simultaneous use of fly ash as a cement main constituent and as a concrete addition to f/c = 0.25.

3.6 Resistance to freeze-thaw with and without de-icing salt

With damage caused by freeze-thaw attack a distinction is made between external and internal damage. External damage is apparent in the form of surface scaling. Internal damage to the microstructure can be determined by

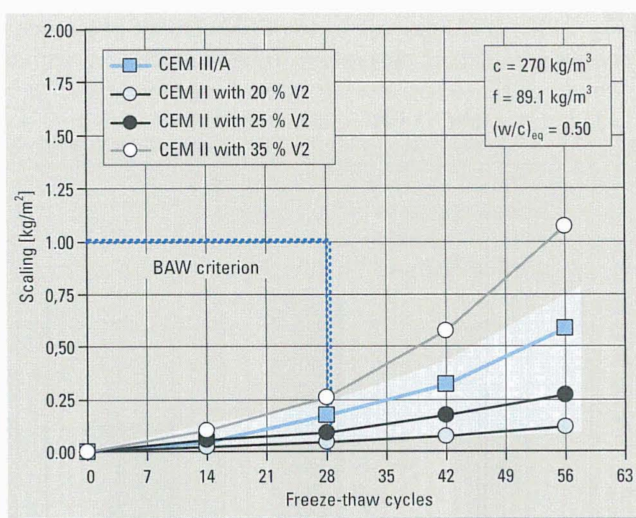

Figure 5: Scaling of concretes (B1*) made with Portland-fly ash cements and reference cement CEM III/A and fly ash as an addition as a function of the number of freeze-thaw cycles and of the cement composition (CF method); acceptance criterion: scaling < 1.0 kg/m^2 after 28 freeze-thaw cycles; white area: value range of CEM I concretes, data from the Research Institute

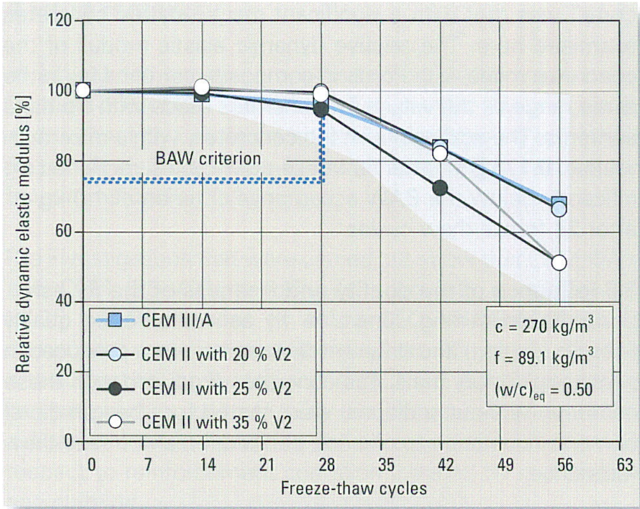

Figure 6: Relative dynamic elastic moduli of concretes (B1*) made with Portland-fly ash cements and reference cement CEM III/A and fly ash as an addition as a function of the number of freeze-thaw cycles and of the cement composition (CIF method); acceptance criterion: relative dynamic elastic modulus > 75 % after 28 freeze-thaw cycles; white area: value range of CEM I concretes, data from the Research Institute

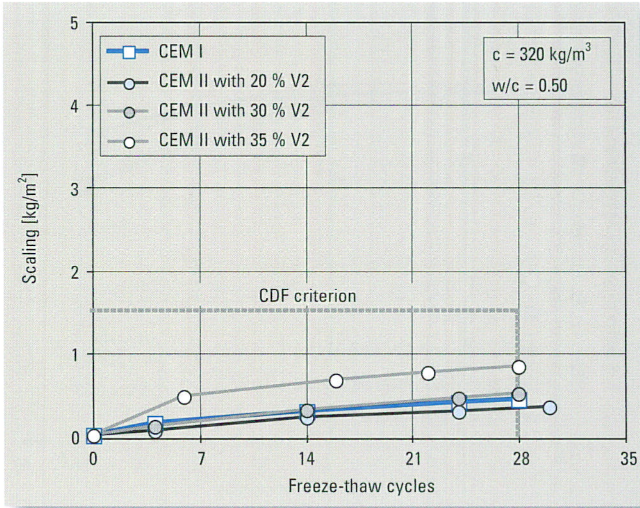

Figure 7: Scaling of air-entrained concretes (B4) made with Portland-fly ash cements and Portland cement as a function of the number of freeze-thaw cycles and the cement composition (CDF method); acceptance criterion: scaling < 1.5 kg/m² after 28 freeze-thaw cycles

measuring the ultrasonic transit time and using this to deduce the dynamic elastic modulus. The results of the tests of the freeze-thaw resistance by the CF/CIF method [11, 12] and the results of the tests of the resistance to freeze-thaw with de-icing salt by the CDF method [11] are described and evaluated below. In Germany the limits for scaling (CF/CDF method) and limits of internal damage to the microstructure (CIF method) are laid down by the BAW (Federal Waterways Engineering and Research Institute) in the instructions on "Freeze-thaw testing of concrete" [13].

In the tests that were carried out the B1* concretes, in which cements containing between 20 wt. % and 35 wt. % fly ash were used in combination with fly ash as a concrete addition (cement content c = 270 kg/m^3, equivalent water/cement ratio $(w/c)_{eq}$ = 0.50, fly ash content f = 89.1 kg/m^3) did not exhibit any significantly higher scalings than the concrete made with the CEM III/A reference cement. ❱ Fig. 5 shows that for all concretes the scaling determined by the CF method remained significantly below the acceptance criterion of 1.0 kg/m^2 after 28 freeze-thaw cycles specified in the instructions on "Freeze-thaw testing of concrete" [13] issued by the BAW. ❱ Fig. 6 shows that after 28 freeze-thaw cycles these concretes exhibited a relative dynamic elastic modulus of more than 75 % (BAW acceptance criteria for the CIF test [13]).

The B1 concretes (without addition) with a cement content of c = 320 kg/m^3 and a water/cement ratio w/c = 0.50 also complied with the BAW criteria by a significant margin when Portland-fly ash cements containing between 20 wt. % and 35 wt. % fly ash were used.

The resistance to freeze-thaw attack with simultaneous exposure to de-icing salt was tested by the CDF test. As a rule a specific de-icing salt solution (3 % NaCl solution) is used. In the testing of the freeze-thaw resistance with de-icing salt of concrete with artificially entrained air voids the surface scaling is dominant and is of prime importance for the assessment. The resistance to freeze-thaw with de-icing salt was tested on concretes (without additions) with a cement content of c = 320 kg/m^3 and a water/cement ratio = 0.50. The results are shown in ❱ Fig. 7. The scaling of the concretes produced with Portland cement and with the cements containing from 20 wt. % to 35 wt. % fly ash lay between 300 g/m^2 and 900 g/m^2 after 28 freeze-thaw cycles, and were therefore significantly below the acceptance criterion [13] of 1500 g/m^2 after 28 freeze-thaw cycles used for this method.

3.7 Granulated blastfurnace slag and limestone as further main constituents in Portland-composite cements containing fly ash

Concretes made with Portland-composite cements that contained granulated blastfurnace slag and/or limestone in addition to clinker and coal fly ash as main constituents were also investigated as part of the research project described here.

The resistance to penetration by chlorides was determined by way of example on concrete B1 with a cement content of c = 320 kg/m^3 and a water/cement ratio w/c = 5.0 (without addition). ❱ Fig. 8 shows the migration coefficients of the concretes that were prepared from the two reference cements and the cements containing fly ash with a total of

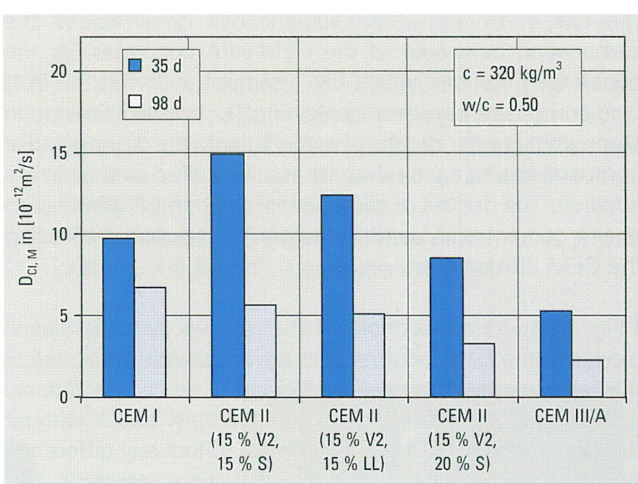

Figure 8: Chloride migration coefficients of concretes (B1) made with Portland-composite cements and reference cements containing fly ash as a function of test age and cement composition

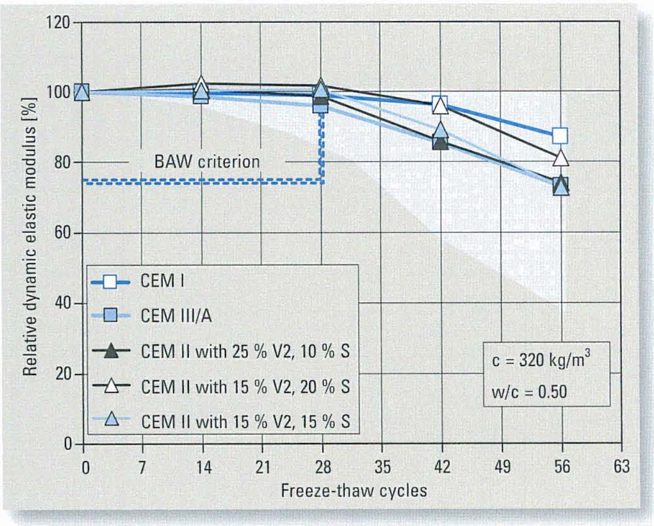

Figure 9: Relative dynamic elastic moduli of concretes (B1) made with Portland-composite cements and reference cements containing fly ash as a function of the number of freeze-thaw cycles and of the cement composition (CIF method); acceptance criterion: relative dynamic elastic modulus > 75 % after 28 freeze-thaw cycles; white area: value range of CEM I concretes, data from the Research Institute

30 wt. % or 35 wt. % fly ash combined with limestone or granulated blastfurnace slag. At a test age of 35 days the concretes made with Portland-composite cements had a maximum chloride migration coefficient of $15 \cdot 10^{-12}$ m^2/s. The increase in the granulated blastfurnace slag content from 15 wt. % to 20 wt. % in the cement in combination with 15 wt. % fly ash as a further main constituent in addition to Portland cement clinker led to a resistance to penetration by chlorides that, at a test age of 35 days, is comparable to that of the CEM I concrete. After 98 days the resistance to penetration of chlorides was of the same order as the CEM III/A concrete (cement containing 50 wt. % granulated blastfurnace slag).

The pore size distributions of the mortars made with CEM I cement and with the Portland-composite cement containing 15 wt. % limestone and 15 wt. % fly ash determined during these investigations were similar. Correspondingly, the B5 concretes (without additions) made using these cements exhibited comparable carbonation characteristics that depended on the age at testing. For the B5* concrete, fly ash was also used as a concrete addition (f = 79.2 kg/m^3). The use of fly ash as an addition had no effect on the carbonation behaviour of the CEM III/A concrete. For the concretes produced with CEM I cement and with the Portland-composite cements containing fly ash and limestone somewhat greater depths of carbonation were determined at comparable test ages when fly ash was used as a concrete addition. The depths of carbonation when the Portland-composite cement was used lay below the values when using the CEM III/A cement.

› Fig. 9 shows an example of the relative dynamic elastic moduli of the B1 concretes with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m^3 (without additions) determined by the CIF method (freeze-thaw attack without de-icing agent). It was not possible to detect any difference between the concretes made with various cements containing fly ash and granulated blastfurnace slag. The acceptance criterion of 75 % after 28 freeze-thaw cycles specified in the BAW instructions on "Freeze-thaw testing of concrete" was met with a significant margin by the concretes examined here. The relative dynamic elastic moduli of the concretes made with Portland-composite cements lay in the same range as the values for concretes made with Portland cements. The scalings from the concretes, with a maximum value of 0.17 kg/m^2 after 56 freeze-thaw cycles, remained significantly below the BAW acceptance criterion of 1.0 kg/m^3 after 28 freeze-thaw cycles.

3.8 Influence of the quality and fineness of the fly ash

Cements containing 30 wt. % fly ash of differing quality (loss on ignition) and different finenesses were produced in some exploratory trials. The concretes produced with these cements (without additions) were tested for strength development, resistance to chloride penetration and freeze-thaw resistance.

The use of different fly ashes (with losses on ignition from 2.9 wt. % to 7.0 wt. %) as cement main constituents did not introduce any significant differences in the concrete investigations. The freeze-thaw resistance can be cited here as an example. The tests using the CF/CIF method on B1 concretes (cement content c = 320 kg/m^3, water/cement ratio w/c = 0.50) using cements containing fly ash V1, V2 or V3 exhibited scalings of 0.09 kg/m^2 to 0.15 kg/m^2 and relative dynamic elastic moduli of 84 % to 92 % after 28 freeze-thaw cycles.

The use of a cement containing 30 wt. % ground fly ash V2 (fineness 4400 cm^2/g Blaine) led to a compressive strength after 28 days and 91 days that was higher by 6 to 9 MPa than with a cement with fly ash in its original state (fineness 3700 cm^2/g Blaine) with the same clinker fineness.

The pore system of the test mortar became finer. The resistance of the concrete produced from this cement to penetration by chlorides increased. As can be seen from › Fig. 10, the chloride migration coefficient of the B1 concrete (cement content c = 320 kg/m^3, water/cement ratio w/c = 0.50) at 35 days reached a value of $20 \cdot 10^{-12}$ m^2/s when using cement with fly ash in its original state. When the cement containing finer fly ash was used the value fell to $12 \cdot 10^{-12}$ m^2/s. Beneficial effects were also apparent in these concretes in the investigations of the freeze-thaw resistance using the CF/CIF methods. There were further reductions in the external and internal damage.

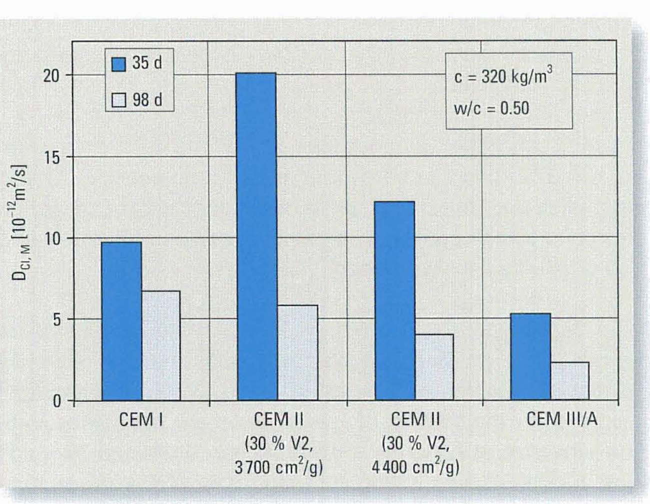

Figure 10: Chloride migration coefficients of concretes (B1) made with Portland-fly ash cements and reference cements as a function of test age and cement composition

4 Final remarks

Investigations into the properties of concretes made using Portland-composite cements that contain fly ash, with and without fly ash as an addition, were carried out at the Research Institute of the Cement Industry. The results can be summarized as follows:

The investigations that were carried out show that CEM II/A-V and CEM II/B-V Portland-fly ash cements containing up to 35 wt. % siliceous fly ash and CEM II/B-M Portland-composite cements containing up to 35 wt. % fly ash and limestone, or fly ash and granulated blastfurnace slag, can be used in concrete with the simultaneous use of fly ash as a concrete addition for all exposure classes with respect to reinforcement corrosion induced by carbonation and chloride.

The results of the investigations into the freeze-thaw resistance, measured by the CF/CIF method, of concrete made using Portland-fly ash cements containing up to 35 wt. % siliceous fly ash and CEM II/B-M Portland-composite cements containing up to 35 wt. % fly ash and granulated blastfurnace slag were as follows:

Even with the high level of water saturation in the CIF test, concretes with a water/cement ratio w/c = 0.50 and a cement content c = 320 kg/m^3 complied with the acceptance criteria for the relative dynamic elastic modulus specified in the "Freeze-thaw testing of concrete" instructions issued by the BAW (Federal Waterways Engineering and Research Institute) of 75 % after 28 freeze-thaw cycles. Furthermore, for all concretes the scaling determined by the CF method remained significantly below the BAW acceptance criterion of 1.0 kg/m^2 after 28 freeze-thaw cycles.

In concretes with an equivalent water/cement ratio $(w/c)_{eq}$ = 0.50 the acceptance criterion of 75 % after 28 freeze-thaw cycles specified in the "Freeze-thaw testing of concrete" instructions issued by the BAW was also met when using Portland-fly ash cements with fly ash as a main cement constituent and simultaneous use of fly ash as a concrete addition.

The scaling behaviour of concretes made with Portland-fly ash cements and artificially entrained air voids in the CDF test (freeze-thaw attack with de-icing salt) was not significantly different from that of the concrete made with Portland cement.

Acknowledgement

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LITERATURE / LITERATUR

[1] Brameshuber, W.; Uebachs, S.; Schießl, P.; Brandes, C.: Anrechnung von Flugasche auf den Wasserzementwert bei Betonen unter Frost-Tausalz Beanspruchung – Teil 1 und 2. beton 55 (2005) H. 1+2, S. 24–31 und H. 3, S. 106–110

[2] Müller, C.: Performance of Portland-composite cements. CEMENT INTERNATIONAL 4 (2006) No. 2, pp. 112–119.

[3] Verein Deutscher Zementwerke: AiF-Abschlussbericht zum Forschungsvorhaben „Dauerhaftigkeit von Betonen unter Verwendung von Zementen mit mehreren Hauptbestandteilen – Teil 2: Zemente mit bis zu 35 M.-% kieselsäurereicher Flugasche" (AiF-Nr. 14012 N)

[4] DIN-Fachbericht 100 „Beton": Zusammenstellung von DIN EN 206-1 Beton – Teil 1: Festlegung, Eigenschaften, Herstellung und Konformität und DIN 1045-2 Tragwerke aus Beton, Stahlbeton und Spannbeton – Teil 2: Beton – Festlegung, Eigenschaften, Herstellung und Konformität – Anwendungsregeln zu DIN EN 206-1. 1. Auflage 2001

[5] Bunke, N.: Prüfung von Beton-Empfehlungen und Hinweise als Ergänzung zu DIN 1048. Schriftenreihe des Deutschen Ausschusses für Stahlbeton, Nr. 422, Beuth Verlag, Berlin 1991

[6] Stark, J.; Wicht, B.: Dauerhaftigkeit von Beton. Hochschule für Architektur und Bauwesen, Weimar 1995

[7] Manns, W.; Thielen, G.; Laskowski, C.: Bewertung der Ergebnisse von Prüfungen zur bauaufsichtlichen Zulassung von Portlandkalksteinzementen. beton 48 (1998) H. 2, S. 779–784

[8] Tang, L.: Chloride Transport in Concrete – Measurement and Prediction. Göteborg, Chalmers University of Technology, Diss., 1996

[9] Ludwig, H.-M.: Entwicklung und Einführung von CEM II-M-Zementen. 15. Internationale Baustofftagung (ibausil), Tagungsband 2, Weimar 2003, S. 2–1415

[10] Gehlen, C.: Probabilistische Lebensdauerbemessung von Stahlbetonbauwerken – Zuverlässigkeitsbetrachtungen zur wirksamen Vermeidung von Bewehrungskorrosion. Schriftenreihe des Deutschen Ausschusses für Stahlbeton, Nr. 510 (Dissertation), Beuth Verlag, Berlin 2000

[11] DIN CEN/TS 12390-9: Prüfung von Festbeton Teil 9: Frost- und Frost-Tausalz-Widerstand/Abwitterung, 2006

[12] Setzer, M.J.; Auberg, R.: Prüfverfahren des Frostwiderstands von Beton: Bestimmung der inneren Schädigung – CIF-Test (Capillary Suction, Internal Damage and Freeze-Thaw Test). Betonwerk und Fertigteil-Technik 64 (1998) H 4, S. 94–105

[13] Bundesanstalt für Wasserbau (BAW): Merkblatt „Frostprüfung von Beton" – Ausgabe Juli 2004