Durability of blended cements with several main components

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Summary

The European cement standard EN 197-1 defines Portland composite cements (CEM II-M) which are characterized by two or more main constituents in addition to clinker. The real advantages of this type of cement are in the combined use of the individual strength of well-established materials. Basic requirement for the application of these cements, which are new in several markets, is the verification of durability of concrete.

In an extensive test program the most important durability aspects were investigated (carbonation, freeze-thaw resistance, frost-de-icing salt resistance, chloride penetration). The program focuses on cements with the combination of granulated blast furnace slag (gbfs) and limestone, but also other combinations (gbfs/fly ash, fly ash/limestone) were included.

The test results clearly indicate that Portland composite cements in the range of the investigated compositions show a high durability. In comparison to ordinary Portland cements and well-known blended cements the results of tested parameters were on a similar level. Thus the existing applications rules can be transferred to Portland composite cements without changes.

1. Principle of “composite cements” or ”ternary blends”

Blended cements usually are composed by clinker, the blending constituents, gypsum and, potentially other minor constituents and additives. The most common blends are granulated blast furnace slag, fly ash and limestone. But there is still the option to use a combination of these additions beside clinker. This kind of mixtures is usually designated as “ternary blends” or “composite cements”.

The option to manufacture cement with several main constituents opens the opportunity to optimize cement properties by the use of the strength of the individual components and to eliminate their weaknesses. Additionally it gives the producer a high flexibility in material selection, in dosage of the individual constituents, and in cement grinding and blending process.

As example, these options should be demonstrated by one cement composed by clinker, granulated blast furnace slag (gbfs) and limestone (Fig.1). Gbfs usually is harder to grind compared to clinker. When ground together, the slag particles cumulate in the coarser fractions of the cement. In contrast, limestone has a better grindability than clinker. Therefore the limestone is enriched in the finer fraction of the particle size distribution. Grinding all three materials together, the different constituents will concentrate in different fractions. As consequence a broader particle size distribution will result which, for example, gives better performance with respect to workability.

Additional process steps like pre-grinding of pre-blending of some components give additional options for quality optimization with respect to the whole range of cement properties and performance.

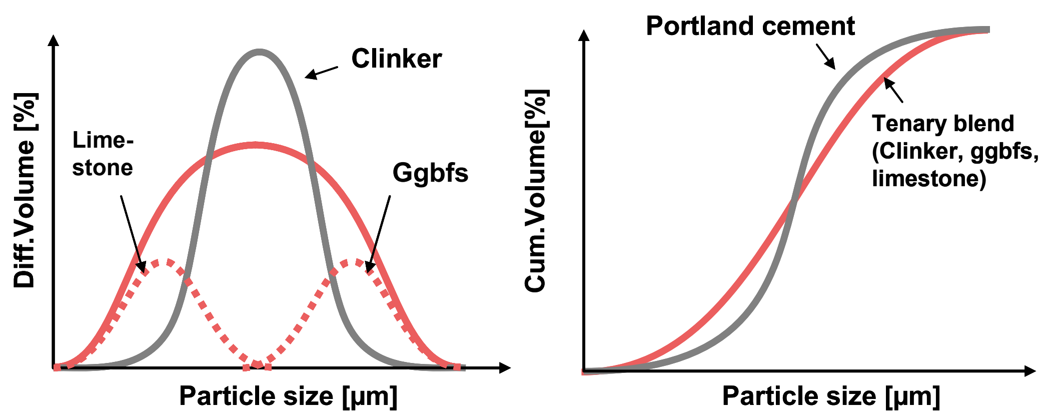

Figure 1: Principle changes in particle size distribution of an interground ternary blend

2. Ternary blends in cement standards

The European cement standard EN 197-1 covers 26 different types of blended cements. Cement types with two or more main constituents in addition to clinker (Table 1) are defined as

- Portland composite cements (CEM II-M) or
- Composite cements (CEM V)

Portland composite cements type CEM II/A-M contain up to 20 % by weight of main constituents others than clinker (each in minimum 6 %), type CEM II/B-M up to 35 %. Most common combinations are slag/limestone (S-LL), slag/siliceous fly ash (S-V), and fly ash/limestone (V-LL) which are covered by this paper. Composite cements of class CEM V are composed of slag and a pozzolan (mainly fly ash). The cement types are defined by a minimum content of each of these constituents (18 % for type CEM V/A, 31 % for type CEM V/B) and a minimum clinker content (Table 1).

Table 1: Composition of composite cements according to EN 197-1

Type	Clinker	Slag S	Pozzolan D, P, Q, V, W	Limestone L, LL
CEM II/A-M	80-94	6-20		
CEM II/B-M	65-79	21-35		
CEM V/A	40-64	18-30	18-30	-
CEM V/B	20-38	31-50	31-50	-

In ASTM blended cements with several components are covered by ASTM C 596 “Standard Specifications for Blended Hydraulic Cements” and by ASTM C 1157 “Standard Performance Specification for Hydraulic Cements”.

Within the definition of Pozzolan Modified Portland cements Type I(PM) ASTM 595 allows the blend of Portland Blast-Furnace Cement (Type IS containing between 25 and 70 % of slag) and less than 15 % of pozzolan. In Portland Pozzolan Cements Type P the pozzolan content is between 15 and 40 %.

ASTM C 1157 specifies Modified Portland Cement (less than 15% addition) and Blended Portland Cements (more than 15% addition) as blends of Portland Cement with one or more additions selected by the manufacturer. Performance requirements are defined according to the intended use of the cements.

3 Test program

As already produced and applied for long time blended cements, containing slag, fly ash or limestone individually, have proven high quality and excellent performance. There is no indication that combinations of two of these components show substantial changes in principle hydration characteristics and structure formation. Thus fundamental changes in concrete properties are not to be expected in any way.

Nevertheless a test program was initiated to prove the most relevant durability properties of concrete containing these types of cement. To get a widespread picture, cements of EN 197-1 type CEM II/B-M from different plants (A to F) were used (Table 2).

Table 2: Composition and standard properties of investigated EN 197-1 type CEM II/B-M cements

CEM II/M-B Type		Composition				Specific surface	Water demand	Initial setting	Compressive strength			
		Clinker	Slag	Lime-stone	Fly Ash				2d	7d	28d	90d
		wt.-%				cm²/g	wt.-%	min	MPa			
S-LL	A	68	17	15	0	5300	26	190	17.5	33.8	48.5	54.6
	B	65	22	13	0	3660	29	190	16.7	36.4	49.7	59.3
	C	69	15	16	0	4580	28	170	19.5	35.8	47.4	57.7
	D	66	21	13	0	4490	28	150	18.7	35.0	48.1	59.9
S-V	E	67	20	0	13	3750	30	270	16.4	31.8	50.4	59.5
V-LL	F	72	0	17	11	5010	28	120	28.7	42.5	50.8	59.7

The differences in composition and the specific surface of the interground cements indicate the differences in production facilities and raw materials which were selected according to the local availability. Nevertheless the 28 day-strength of all cements were in a similar range of 47 to 50 MPa complying with strength class 32.5 R according to EN 197-1. All cements show a further, remarkable strength increase between 28 and 90 days resulted from their latent hydraulic (slag) or pozzolanic (fly ash) constituents.

With these cements concrete tests were performed to investigate the carbonation behavior, the penetration of chloride ions and the resistance to repeated cycles of freezing and thawing as well to de-icing salt scaling. For each test criterion concretes of different composition were designed to allow better comparison to existing testing procedures (Table 3). Also curing conditions were adjusted to these procedures.

Table 3: Concrete composition and curing of concrete for different durability tests

Test	Concrete composition					Curing
	Cement	Water	w/c	max.aggr. size	Air void	
	kg/m³	l/m³		mm	vol.-%	
Carbonation	500	250	0.50	8	~ 2.0	1d in mould, 6d under water (20°C) 1d in mould, 27d under water (20°C)
Cl migration	320	160	0.50	16	~ 2.0	1d mould, then under water (20°C) until testing
Freeze-thaw	300	180	0.60	32	~ 2.0	1d in mould, 6d under water (20°C), then climate 20°C/65 % r.h. until testing
Frost de-icing	320	160	0.50	16	~4.5	1d in mould, 6d under water (20°C), then climate 20°C/65 % r.h. until testing

4 Carbonation

The progress of carbonation mainly depends on the diffusion of CO_2, the CO_2 binding capacity of hardened cement paste and the humidity level in concrete. Usually the carbonation rate increases with decreasing content of $Ca(OH)_2$ generated during cement hydration. Fig.2 exemplarily shows the development of $Ca(OH)_2$ content for 2 different cements CEM II/B-M compared to an Ordinary Portland cement (CEM I) and a Blastfurnace cement CEM III/A (containing 50% of slag).

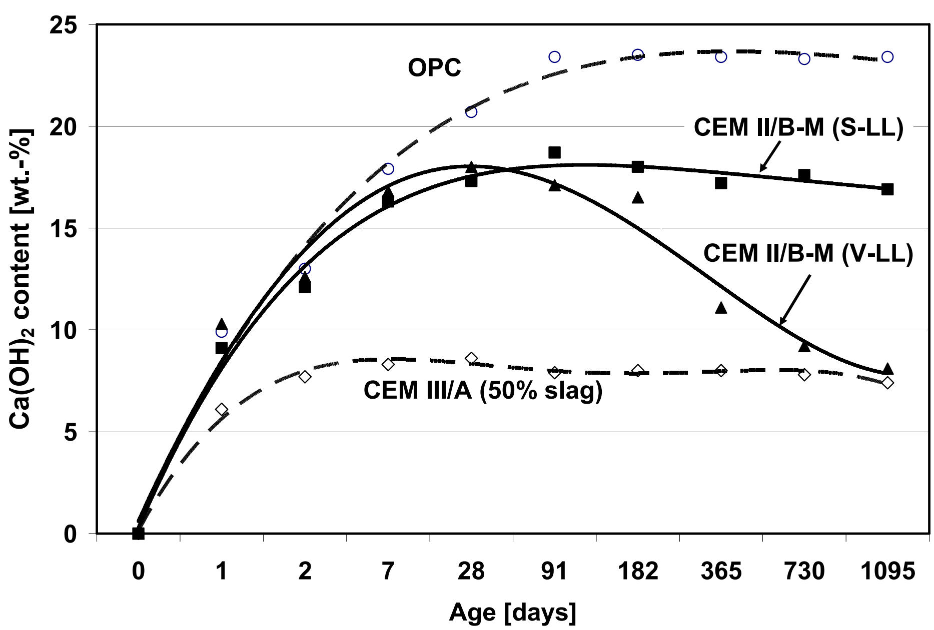

Figure 2: Development of $Ca(OH)_2$ in cement paste (mortar, w/c = 0.60; cured at 20°C under water until testing)

The $Ca(OH)_2$ content of the cement containing slag and limestone (S-LL) is on a level about 25 to 30% lower than that of CEM I. This corresponds to the amount of slag and limestone substituting clinker. As blast furnace slag only consumes a small amount of $Ca(OH)_2$ during its reaction, the reduction of $Ca(OH)_2$ is mainly due to a “clinker diluting” effect. The cement containing fly ash and limestone (V-LL) shows the same development up to 28 days. Hereafter the pozzolanic reaction of fly ash becomes efficient considerably characterized by a further consumption of $Ca(OH)_2$. This reaction progresses over a longer period. Nevertheless it does not drop below the level of the Blastfurnace cement which is a in practice well proven cement also concerning carbonation.

The remaining content of $Ca(OH)_2$ is also sufficient to ensure the high level of alkalinity which is necessary to protect the embedded steel reinforcement against corrosion.

The depth of carbonation was test on standard mortar prisms produced according to EN 196-1. After demoulding the samples were cured under water (20°C) up to 7 or 28 days respectively. Then they were stored in laboratory climate of 20°C, 65% of relative humidity and atmospheric carbon dioxide concentration. The usual procedure for measuring the depth of carbonation on freshly crushed surfaces sprayed with phenolphthalein solution was used.

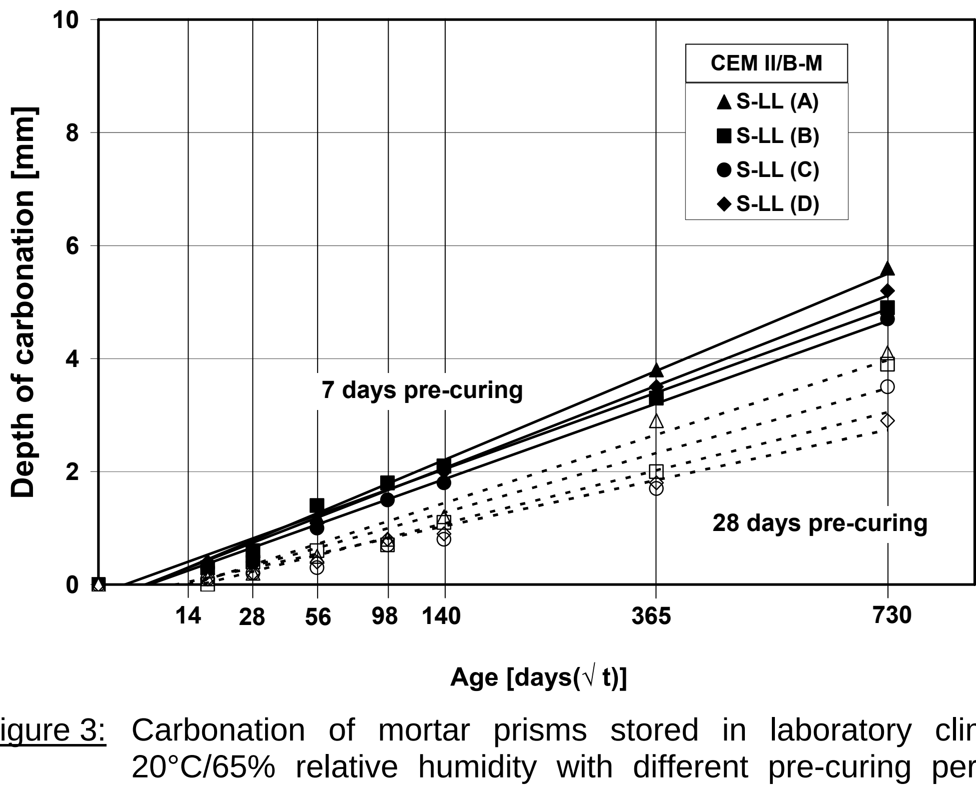

Figure 3: Carbonation of mortar prisms stored in laboratory climate 20°C/65% relative humidity with different pre-curing periods (concrete. max. aggregate size 8 mm; cement content 500 kg/m³, w/c = 0.50)

Fig.3 shows the development of carbonation of the composite cements containing slag and limestone. As to be expected, the samples with longer curing exhibit lower carbonation. Indicating the dependence on a diffusion process there is a linear relationship between the square root of time and the depth of carbonation. In principle, there are no significant differences between the 4 cements.

As there is no agreed or standardized test procedure, any generally accepted limit values or test criteria for evaluating the carbonation progress do not exist. Differences in the most relevant parameters like sample composition, curing and storage conditions in many cases do not allow the direct comparison to other results. But the available experiences with the carbonation behaviour of other common blended cements indicate no deviating performance of the investigated composite cements.

5 Chloride penetration

The determination of real chloride diffusion coefficients of concrete usually is time consuming and complex. To get useful information already in short time, the Rapid Chloride Migration Test (RMC Test) was applied according to a procedure developed by [1]. In this method the transport of chloride ions is accelerated by an electric currency (about 30 V). Water saturated concrete slices (diameter 100 mm, thickness 50 mm) were mounted in a measurement device separating the anodic and cathodic part of sample.

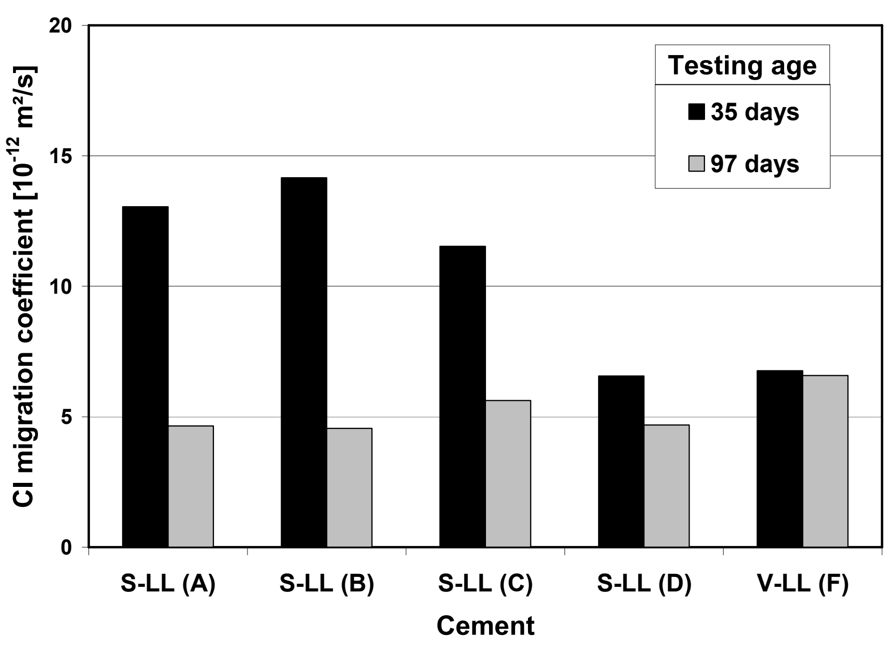

Figure 4: Results of Rapid Chloride Migration Test of samples tested at age of 35 and 97 days respectively (concrete composition: cement content 320 kg/m³, w/c = 0.50)

The cathodic part was submerged with 3% chloride solution and put under currency for about 24 hours. Afterwards the concrete slices were split and the ingress of chlorides was visualized and measured by spraying the crushed surface with an indicator ($AgNO_3$ solution).

Fig. 4 shows the test results for concrete samples tested at an age of 35 and 97 days respectively. According to the progressing hydration the migration coefficients are decreasing with longer curing period. The values for cement S-LL(A), (B) and (C) are in the range of 10 to $15 \cdot 10^{-12}$ m²/s after 35 days and go down to a lever of about $5 \cdot 10^{-12}$ m²/s. The coefficients for cements S-LL(D) and V-LL(F) are already very low at 35 days, so there is only limited further reduction.

For the time being there are no generally accepted criteria to evaluate of test results. Current experiences show that chloride migration coefficients of concretes with ordinary Portland cement (w/c = 0.50) are in the range of 10 to $25 \cdot 10^{-12}$ m²/s. All measured concrete samples with cements CEM II/B-M are within or below that range indicating a good performance in limiting the penetration of chlorides.

6 Resistance to freeze-thaw cycles

For testing the resistance against freeze-thaw cycles various test methods are in use. Here the cube test was applied which is specified as alternative method in the current draft of the European pre-standard prEN 12390-9 [2]. Two 10 mm concrete cubes, immersed in de-ionised water, are subjected to 100 freeze-thaw cycles starting at an age of 28 days. During each cycle the concrete cubes are cooled down in a given time pattern from +20°C to -20°C within 16 hours. Afterwards the containers with the cubes are stored in a water bath of +20°C for 8 hours before the next cycle starts. The mass loss of the cubes is measured after 10, 25, 50, 75 and 100 freeze-thaw cycles by weighing the scaled concrete pieces after drying.

As the concrete samples are immersed under water during the whole test, the procedure is very strong. Nevertheless the scaling of all concretes containing cements CEM II/B-M was rather low (Fig.5). Having in mind the usual variability of freeze-thaw test, there are no significant differences between the different cements. The comparison with results from concretes produced with Portland cement (EN 197-1 CEM I) indicate the good performance of the concretes with cements CEM II/B-M. Existing experiences show that concretes with a composition as tested here are classified to have a very high resistance when the scaling is below 5 % by weight after 100 cycles.

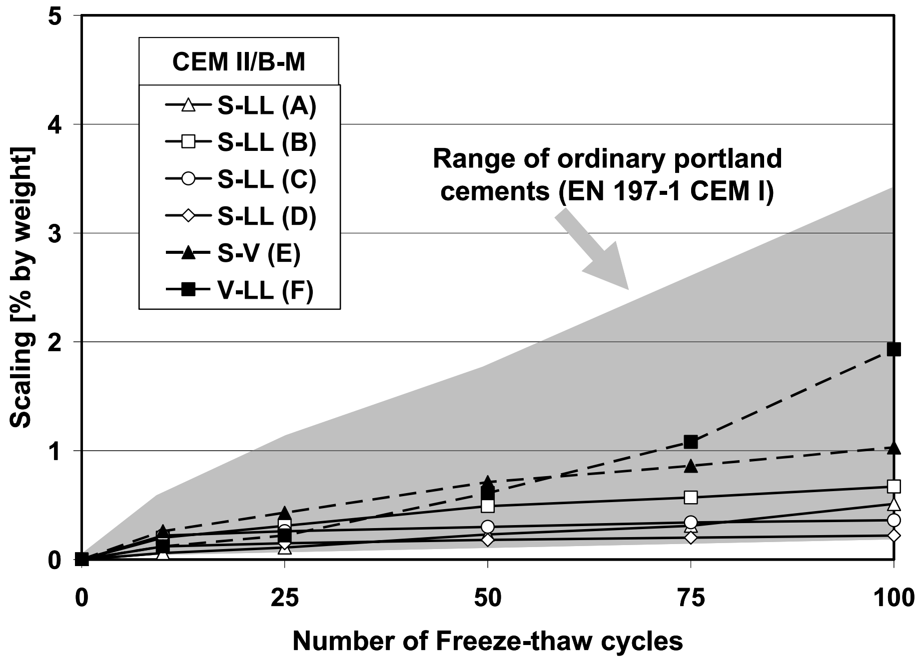

Figure 5: Development of scaling of concretes exposed to freeze-thaw cycles (concrete composition: cement content 300 kg/m³, w/c = 0.60, no air entrainment)

7 Resistance to de-icing salts

The resistance against combined attack against freezing and de-icing agents was tested according to the CDF procedure [3]. Two specimens, made by splitting a 150 mm cube with a centralised PTFE plate in the mould, are subjected to freeze-thaw attack in presence of a 3 % sodium chloride solution at 28 days after 7 days wet and 21 days dry curing. The specimens are placed in the test containers with the test surface downwards to allow capillary suction for additional 7 days. Then freeze-thaw cycles started where the cooling liquid passes a defined temperature range from +20°C to -20°C within 12 hours. The freeze-thaw scaling resistance is evaluated by the mass measurement of pieces scaled from specimens after 4, 14 and 28 freeze-thaw cycles.

The scaling of the air entrained concretes produced with cements CEM II/B-M (S-LL) and (V-LL) are all in the range between 200 and 600 g/m² after 28 cycles (Fig.6). There are no significant differences between these cements having in mind the usual variability of test procedure. The scaling increases nearly linear with the number of cycles. There is no higher scaling rate at the first number of cycles indicating a proper structure of the concrete surface layer with low carbonation.

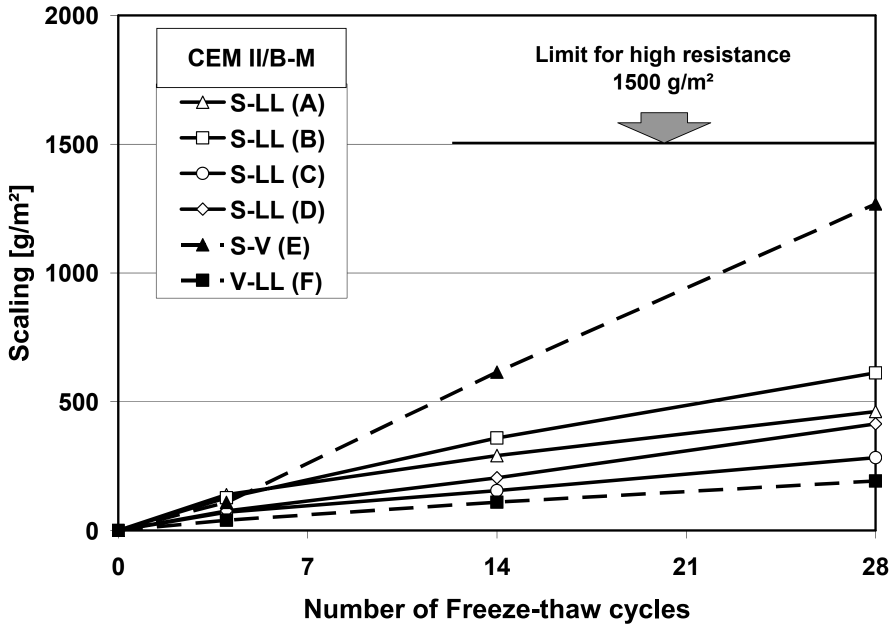

Figure 6: Development of scaling of concretes exposed to freeze-thaw cycles and de-icing salts (concrete composition: cement content 320 kg/m³, w/c = 0.50, 4.5 % air entrainment)

Only the concrete with cement CEM II/B-M containing a combination of slag and fly ash showed a higher scaling compared to the other cements. Due to the fact that this is a single sample of this cement type tested, the result could not be generalized. Nevertheless, scaling is clearly below the widely accepted limit of 1500 g/m² for concretes exhibiting a high resistance against combined freeze-thaw and de-icing salt attack.

8 Conclusions

From a larger program the most important results concerning the durability of concretes produced with cements containing different mixes of slag, fly ash and limestone (ternary blends) were presented. The test results clearly indicate that Portland composite cements in the range of the investigated compositions show a high durability. In comparison to ordinary Portland cements and well-known blended cements the results of tested parameters were on a similar level. Thus the existing applications rules can be transferred to Portland composite cements without changes.

Literature

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[3] RILEM Recommendation TC 117-FDC: Freeze-thaw and deicing resistance of concrete. Materials and structures 29 (1996) S.523-528