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SUMMARY

The manufacture of cements with several main constituents is of particular importance with regard to reducing climatically relevant CO_2 emissions in the cement industry. Investigations focusing on the performance of these cements therefore constitute one of the key research topics at the Research Institute of the Cement Industry in Düsseldorf, Germany. This ecological aspect is not the only argument in favour of Portland-composite cements. They are also viable alternatives to Portland cement from the technical point of view. However, in some cases these cements, which comply with EN 197-1, are excluded in parts of Europe from use in certain exposure classes because of the lack of building experience within the scope of the respective national annexes to concrete standard EN 206-1 and because there have been no scientific investigations into the use of these cements. Evidence of suitability for application in certain exposure classes can be supplied in these cases in Germany through national technical inspectorate approvals. Some German cement manufacturers have developed new CEM II-M cements for which initial technical approvals have been granted. The influence exerted by different main constituents of cement on concrete properties is discussed on the basis of a comparison between concrete made from Portland cement and concretes made from cements containing, for example, limestone or blastfurnace cements. No cement – not even Portland cement – provides the perfect solution for all areas of application. The comparison shows that the advantages and disadvantages of the different main constituents for the properties of concrete, which extend from workability via strength development to durability characteristics, are distributed fairly evenly. The option of combining several main constituents makes CEM II-M Portland-composite cements particularly well suited for counterbalancing the advantages and disadvantages of individual main constituents, and thus for developing these cements into even more robust systems. This process requires an integrated assessment of all requirements to be met by cements during manufacture and application. From a technical perspective these include the strength formation potential as well as good workability of the concrete and, in particular, the durability of the concrete made from these cements. From the cement manufacturers' point of view the ratio of the cost of production to the price of the cement in the market plays a role as well, as do environmental aspects. The compensatory effects that the main constituents have with regard to properties relevant to durability can be utilized in particular in cements made from a combination of limestone/blastfurnace slag or limestone/fly ash as main constituents. This is demonstrated using the parameters of density, carbonation, resistance to chloride penetration, resistance to freeze-thaw and resistance to freeze-thaw with de-icing salt.

ZUSAMMENFASSUNG

Im Hinblick auf die Verminderung der klimarelevanten CO_2-Emissionen in der Zementindustrie kommt der Herstellung von Zementen mit mehreren Hauptbestandteilen eine besondere Bedeutung zu. Untersuchungen zur Leistungsfähigkeit dieser Zemente sind daher einer der Forschungsschwerpunkte im Forschungsinstitut der Zementindustrie in Düsseldorf. Nicht nur der ökologische Aspekt spricht für Portlandkompositzemente. Sie sind auch in technischer Hinsicht eine gute Alternative zum Portlandzement. In einigen Fällen aber sind diese Zemente, die EN 197-1 entsprechen, in Europa regional von der Anwendung in bestimmten Expositionsklassen ausgeschlossen, weil im Regelungsbereich des jeweiligen nationalen Anhangs zur Betonnorm EN 206-1 die baupraktischen Erfahrungen fehlen und keine wissenschaftlichen Untersuchungen zur Anwendung der Zemente vorliegen. In diesen Fällen kann in Deutschland der Nachweis der Eignung für die Anwendung in bestimmten Expositionsklassen im Rahmen einer allgemeinen bauaufsichtlichen Anwendungszulassung erbracht werden. Einige deutsche Zementhersteller haben neue CEM II-M-Zemente entwickelt, für die erste bauaufsichtliche Zulassungen erteilt wurden. Der Einfluss verschiedener Hauptbestandteile des Zements auf die Eigenschaften von Beton wird anhand des Vergleichs von Portlandzementbeton mit Betonen z. B. unter Verwendung kalksteinhaltiger Zemente oder von Hochofenzement diskutiert. Kein Zement – auch nicht der Portlandzement – stellt in allen Anwendungsfällen die optimale Lösung dar. Der Vergleich zeigt, dass die Vor- und Nachteile verschiedener Hauptbestandteile auf die Eigenschaften des Betons – von der Verarbeitbarkeit über die Festigkeitsentwicklung bis hin zu Dauerhaftigkeitskenngrößen – relativ gleich verteilt sind. Portlandkompositzemente CEM II-M bieten hier in besonderer Weise die Möglichkeit, durch die Kombination mehrerer Hauptbestandteile die individuellen Vor- und Nachteile einzelner Hauptbestandteile auszugleichen und damit die Zemente zu noch robusteren Systemen weiter zu entwickeln. Dabei müssen alle Anforderungen an den Zement bzgl. Herstellung und Anwendung ganzheitlich betrachtet werden. Hierzu zählt in technischer Hinsicht neben dem Festigkeitsbildungspotenzial und einer guten Verarbeitbarkeit des Betons insbesondere die Dauerhaftigkeit des mit diesem Zement hergestellten Betons. Aus der Sicht des Zementherstellers spielen darüber hinaus das Verhältnis der Produktionskosten zu den am Markt erzielbaren Preisen und Umweltaspekte eine Rolle. Ausgleichende Effekte der Hauptbestandteile im Hinblick auf dauerhaftigkeitsrelevante Eigenschaften können insbesondere bei Zementen mit den Kombinationen der Hauptbestandteile Kalkstein und Hüttensand sowie Kalkstein und Flugasche genutzt werden. Dies wird anhand der Parameter Dichtheit, Carbonatisierung, Chlorideindringwiderstand, Frost- und Frost-Tausalz-Widerstand gezeigt.

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*) Revised text of lecture given to the Technical and Scientific Cement Conference 2005 held by the German Cement Works Association in Nürnberg on 27th and 28th October 2005.

(Translation by Mr. Robin B. C. Baker)

*) Überarbeitete Fassung eines Vortrags, der auf der technisch-wissenschaftlichen Zementtagung 2005 des VDZ am 27. und 28. Oktober 2005 in Nürnberg gehalten wurde.

Performance of Portland-composite cements*)

Leistungsfähigkeit von Portlandkompositzementen*)

1 Introduction

The cement industry is one of the most energy-intensive branches of industry. Energy costs account for a high proportion of the production costs of cement so efforts are always being made for economic reasons to reduce the demand for fuels and electrical energy. A further aspect was added to this at the start of the 1990s with the requirement for specific climate protection aims. The German cement industry, together with other energy-intensive industries, has pledged to make a contribution to climate protection. The process engineering potential for CO_2 abatement by further optimization of state-of-the-art kiln and grinding plants is practically exhausted so, in addition to the use of secondary fuels, particular importance is being placed on producing cements with several main constituents – e.g. Portland-composite cements. By reducing the clinker content by using other main constituents these cements offer an opportunity to lower the specific CO_2 emissions per tonne of cement during the production of cement.

The European cement standard EN 197-1 uses the term "Portland-composite cement" in two respects (❱ Table 1). Firstly, it is used as a generic term for the entire group of CEM II cements. These include, for example, the CEM II-S Portland-slag cements with 6 to 20 or 21 to 35 wt.% granulated blastfurnace slag. This category of cement also includes

- Portland-silica fume cement,
- Portland-pozzolana cement,
- Portland-fly ash cement,
- Portland-burnt shale cement, and
- Portland-limestone cement,

which each has one other main constituent in addition to Portland cement clinker. The term "Portland-composite cement" is also used for the CEM II-M cements in which all the above-mentioned main constituents, that is

- granulated blastfurnace slag,
- silica fume,
- natural pozzolana, e.g. trass,
- siliceous or calcareous fly ash, and
- limestone

can be combined with one another.

This article deals in particular with the properties of CEM II-M cements made using Portland cement clinker, granulated blastfurnace slag and limestone as the main constituents, and with the concretes produced from them.

2 Cement market and application regulations

❱ Fig. 1 provides an overview of the cements produced in Germany. Comparison with the overall European situation is provided by the CEMBUREAU data shown in ❱ Fig. 2.

In Germany about 60 % of the domestic cement sales are Portland cement. Blastfurnace cements account for about 11 % and other cements for about 1 %, leaving a market share of about 30 % for Portland-composite cements. In Europe as a whole the ratio between Portland cements and Portland-composite cements is reversed. The figures are 32 % Portland cement as against about 55 % Portland-composite cement. In the 32,5 strength classes the balance between Portland cements and Portland-composite cements is about even in Germany.

In Europe, on the other hand, about 70 wt.% of all cements in this strength class are Portland-composite cements and only about 10 wt.% of the cements are produced as Portland cement. In Germany about 44 wt.% of the Portland-composite cements CEM II are produced as Portland-slag cements and about 54 wt.% as Portland-limestone cements. The remaining 2 wt.% of the domestic sales are accounted for by Portland-pozzolana cement, Portland-oil shale cement and also – since 2004 – CEM II-M Portland-composite cements CEM II. In Europe as a whole, however, according to CEMBUREAU 35 wt.% of the Portland-composite cements CEM II were produced as CEM II-M cements in 2003.

However, in some cases these cements, which comply with EN 197-1, are excluded in parts of Europe from the use in certain exposure classes because of the lack of building experience within the scope of the respective national annexes to concrete standard EN 206-1 and because there have been no scientific investigations into the use of these cements (Table 2). The table provides an overview of the possible applications of cements complying with EN 197-1 for usual external components in building construction without appreciable external exposure to chlorides. The information was gathered from various sources.

Table 1: Portland-composite cements conforming to EN 197-1

Portland-composite cement	**Portland-slag cement**	CEM II/A-S	6 to 20 wt.%	Granulated blast-furnace slag S
		CEM II/B-S	21 to 35 wt.%	
	Portland-silica fume cement	CEM II/A-D	6 to 10 wt.%	Silica fume D
	Portland-pozzolana cement	CEM II/A-P/Q	6 to 20 wt.%	Natural: P natural calcined: Q
		CEM II/B-P/Q	21 to 35 wt.%	
	Portland-fly ash cement	CEM II/A-V/W	6 to 20 wt.%	Siliceous: V Calcareous: W
		CEM II/B-V/W	21 to 35 wt.%	
	Portland-burnt shale cement	CEM II/A-T	6 to 20 wt.%	Burnt shale T
		CEM II/B-T	21 to 35 wt.%	
	Portland-limestone cement	CEM II/A-L/LL	6 to 20 wt.%	TOC ≤ 0.50 wt.%: L TOC ≤ 0.20 wt.%: LL
		CEM II/B-L/LL	21 to 35 wt.%	
	Portland-composite cement	CEM II/A-M	6 to 20 wt.%	S + D*) + P + Q + V + W + L + LL
		CEM II/B-M	21 to 35 wt.%	

*) 6 to 10 wt.%

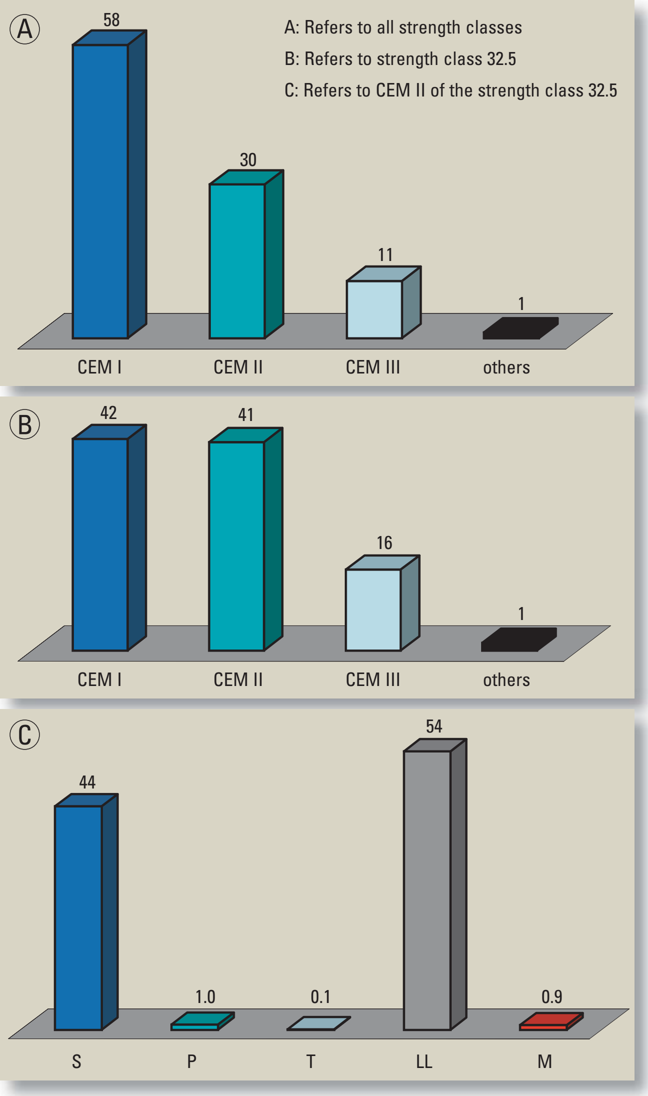

Figure 1: Domestic sales of cement by members of the Federal German Association of the Cement Industry according to type, in wt.% (2003/2004) [1]

The sometimes substantial differences in the cement usage in the concrete standards of the different European states based on EN 206-1 can be seen very clearly. This reflects not only the traditionally different factors of the market and building practice but also different philosophies in setting regulations. For example, specifications are given in the German application standard DIN 1045-2 for the application of all 27 basic types of cement and also for a number of CEM II-M cements but other national annexes to EN 206-1 regulate the application of only a few types of cement that traditionally play a part in the particular national market.

In cases where a cement has been excluded from an application it is possible in Germany to provide evidence of suitability for application in certain exposure classes within the framework of a national technical approval. For the application of the cement some German cement producers have developed new CEM II-M cements for which initial technical approvals have been granted.

3 Why CEM II-M cements ?

What are the particular arguments in favour of CEM II-M Portland-composite cements? From the technical point of view the requirements when developing a new cement include not only the strength-forming potential and good workability but also, and in particular, the durability of the concrete produced from the cement. From the point of view of the cement producer costs and possible environmental aspects naturally also play a part. From the technical point of view, CEM I, CEM II and CEM III cements sometimes have different properties and the concretes made using these cements exhibit different characteristics in laboratory trials and – depending on the property being examined – also in practice. No cement – not even Portland cement – represents the optimum solution in all applications. This is shown diagrammatically in ❫ Fig. 3 for two types of cement with several main constituents compared with Portland cement (black line), which is used as the reference variable. CEM II-M cements provide a particular opportunity to balance the individual advantages and disadvantages of single main constituents by combining several main constituents, thereby developing the cements into even more robust systems. This means that in addition to the aspects of CO_2 abatement and the conservation of resources these cements offer outstanding opportunities for optimizing properties that are relevant to applications – such as workability, strength development and durability.

4 Performance of Portland-composite cements

4.1 General

A series of investigations were carried out at the Research Institute of the Cement Industry – in some cases in co-operation with the FEhS (Institute for Building Materi-

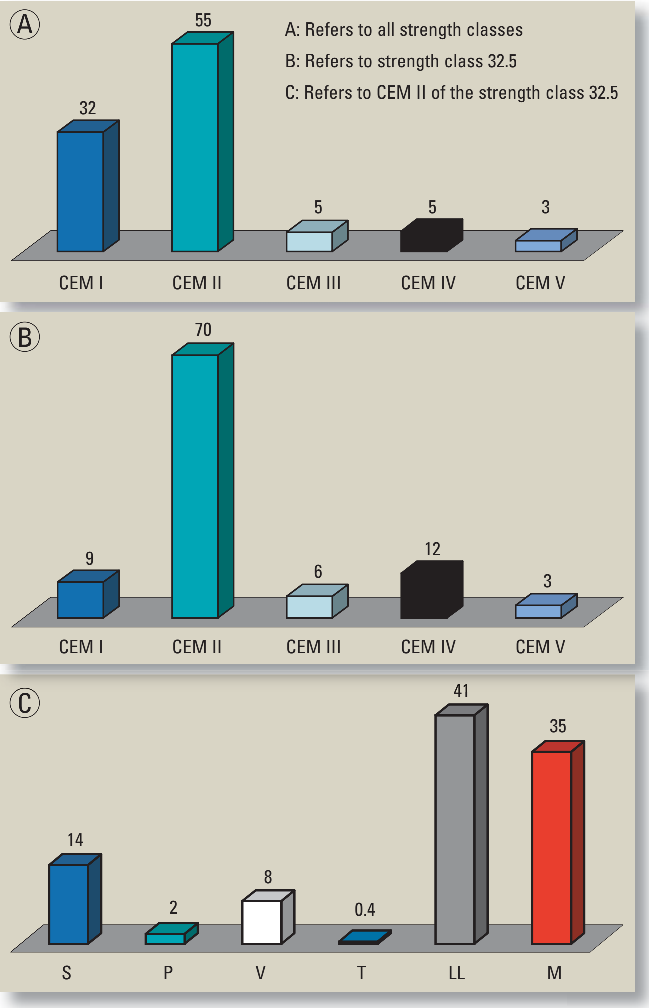

Figure 2: Sales of cement in CEMBUREAU countries in wt.% (2003) – Source: CEMBUREAU

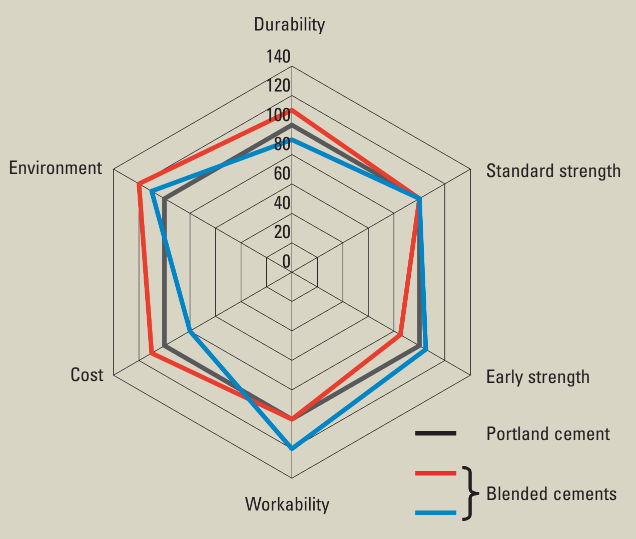

Figure 3: Diagrammatic representation of the influence of the cement type on different parameters [5]

als Research) – into the durability of concretes made with CEM II-M cements. These investigations were intended to contribute to the fact that, due to increasing practical experience with cements holding approvals for certain applications in Germany, the need for such approvals could be dropped in the long-term by changing the German application rules in the standard.

4.2 Porosity and pore size distribution

Porosity and pore size distribution are of fundamental importance for practically all properties of cement-bonded building materials that are relevant to durability This is because, as a rule, harmful influences find their way into the building material through the pore system. The resistance of the concrete to penetration by harmful substances, i.e. the impermeability of the concrete, therefore plays a special role in its durability.

❱ Fig. 4 shows the values, relative to the values for Portland cement, of the total porosity and of the pore fractions < 0.01 µ, i.e. the gel pores, and the pore fractions > 0.1 µ, i.e. the pores that are, for example, relevant to the penetration of CO_2, for various cements with several main constituents. The investigations were carried out on hardened cement paste that had been stored under water for a period of 90 days. With cements containing limestone with a fairly high limestone content the microstructure of the hardened cement paste tends to be somewhat coarsened. However, presupposing adequate curing, there is partly a significant displacement of the pore inlet radius distribution determined with mercury intrusion porosimetry towards finer pores when latent-hydraulic or pozzolanic cement main constituents, such as granulated blastfurnace slag or fly ash, are used. This means, for example, that the opposite effect of limestone can be partially offset by combining granulated blastfurnace slag and limestone. Fig. 4 shows this for a CEM II/B-M (S-LL) cement containing 25 wt.% limestone and 10 wt.% granulated blastfurnace slag. The effect is correspondingly increased with higher levels of granulated blastfurnace slag and lower levels of limestone. These changes to the pore structure act to a greater or lesser extent on the different variables that are relevant to durability.

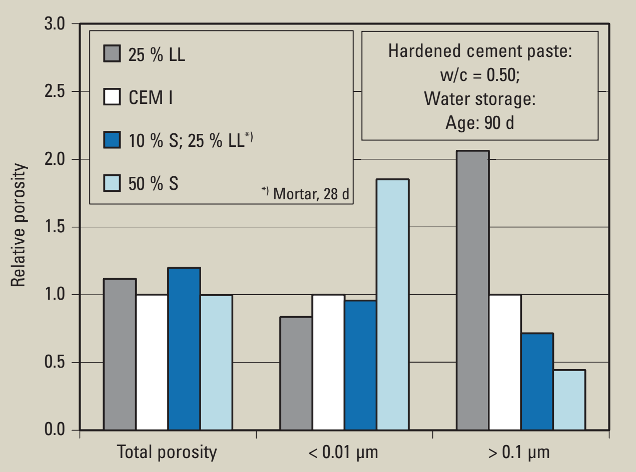

Figure 4: Relative porosity and pore size distribution of hardened cement paste made with different cements containing limestone (LL) and granulated blastfurnace slag (S) compared with hardened cement paste made with Portland cement (CEM I = 100 %). Data: [6, 7]

4.3 Carbonation

The rate and depth of carbonation are dependent not only on the water/cement ratio as the controlling variable but also on the clinker content of the cement in the concrete. The rate of carbonation of concrete made with blastfurnace cements is therefore somewhat higher than that of Portland cement concrete in laboratory trials in a climate of 20 °C and 65 % relative air humidity. This can be seen from the value range shown in ❱ Fig. 5, the upper limit of which represents the values for concretes made with blastfurnace cements. The fact that these differences of the depths of carbonation measured under laboratory conditions are of only secondary importance in practice is shown by the fact that blastfurnace cements containing up to 80 wt.% granulated blastfurnace slag (CEM III/B) are also allowed to be used in concrete for exposure class XC, i.e. where there is a risk of carbonation-induced reinforcement corrosion (see Table 2). As a rule with exterior building components this lies at significantly smaller depths of carbonation in comparison to laboratory storage due to the higher moisture content of the concrete. With interior building components, on the other hand, only a slight risk of corrosion can be assumed in spite of greater depths of carbonation because of the low moisture content. In both cases EN 206-1 is based on a minimum useful life of about 50 years.

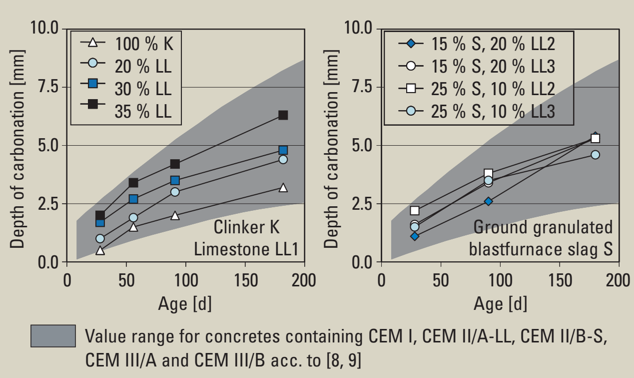

Figure 5: Development with time of the depth of carbonation in concretes with w/c = 0.65 and c = 260 kg/m^3 made using Portland cement and Portland-limestone cements (left) and various Portland-composite cements (right)

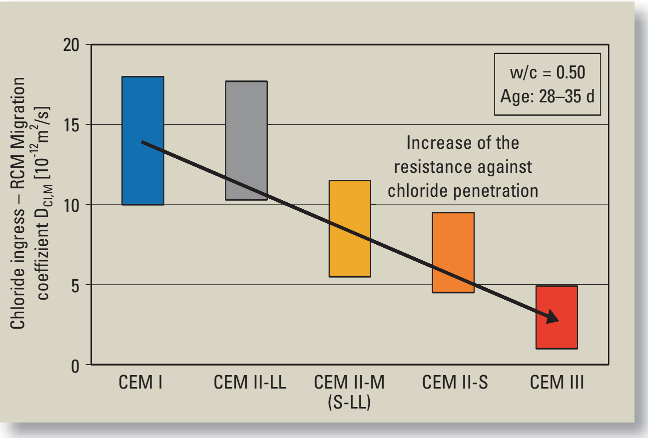

Figure 6: Chloride migration coefficient $D_{Cl,M}$ of concretes with w/c = 0.50 and c = 320 kg/m³ – water storage

In comparison with Portland cement concrete the depth of carbonation in the concrete increases with increasing limestone content. However, even with 35 wt.% limestone the values still lie in the range of those cements that are permitted for unrestricted use in concrete for the XC exposure class, i.e. where there is a risk of reinforcement corrosion initiated by carbonation. By combining limestone and granulated blastfurnace slag – in this case in proportions of 15 and 25 wt.% granulated blastfurnace slag with 20 or 10 wt.% limestone respectively – the concretes (in each case with a cement clinker content of 65 wt.%) exhibit a moderate increase in depth of carbonation that – as with blastfurnace cements – is largely unimportant for practical purposes. The same also applies, for example, to CEM II/B-M (S-V) or (V-LL) Portland-composite cements.

4.4 Resistance to chloride penetration

In practice concretes often come into contact with soils or water containing chlorides. Examples of this are road bridges, the floors of multi-storey car parks and marine structures. Differences in chloride penetration resistance between concretes made with different cements can be detected in laboratory trials and also – assuming adequate curing – in practice. Due to the refinement of the pore system the use of cements containing granulated blastfurnace slag leads in some cases to significant increases in the resistance of the concrete to the penetration of chlorides, i.e. to a reduction in the diffusion coefficient of chloride ions [e.g. 10]. This effect appears very clearly above about 40 wt.% granulated blastfurnace slag, i.e. with the use of CEM III/A cements. In accordance with the German regulatory codes [11] this can be utilized in concretes for massive components in away that the maximum permissible water/cement ratio can be increased from 0.45 to 0.50 when using a CEMIII/A or CEM III/B cement in the XD3 and XS3 exposure classes.

❱ Fig. 6 shows the chloride migration coefficients, determined in an accelerated test, that are also a measure of the resistance to chloride penetration. For the chosen concrete composition the value range for Portland cement concretes usually extends from 10 to 18 x 10^{-12} m²/s. The values for high sulfate-resisting Portland cements may be somewhat higher. The values obtained for Portland-limestone cements depend on the limestone content but lie in the same range as for Portland cements, while the value range for Portland-composite cements using limestone and granulated blastfurnace slag lies between the lower limits for Portland cements and Portland-slag cements.

4.5 Freeze-thaw resistance

Portland cements can be used without restriction under all the climatic conditions covered in the European concrete standard EN 206-1. With pure freeze-thaw attack the same applies to cements containing granulated blastfurnace slag and to blastfurnace cements up to a slag content of 80 wt.% as specified in the German application standard DIN 1045-2. The use of these cements is approved for all components exposed to frost, regardless of the slag content or water saturation of the concrete.

The left-hand side of ❱ Fig. 7 shows the value range of the scaling loss of concretes made with Portland cements and blastfurnace cements when concretes of the given composition are tested by the CF test. The scaling losses of concretes made with different Portland-composite cements with up to 35 wt.% granulated blastfurnace slag and limestone lie in this range and therefore also have a high freeze-thaw resistance. These investigations do not permit any further differentiation between the individual results on the basis of the respective cement compositions.

The relative dynamic elastic modulus is usually determined nowadays in freeze-thaw tests although the applicability of this parameter to practical conditions has not yet been sub-

Table 2: Areas of application of cements conforming to EN 197-1 in concrete conforming

Country	Exposure class	min f_c	max $(w/c)_{eq}$	min c kg/m³	CEM I
Austria	XC1+XF1	–	0.55	300	x
Belgium	EE3 (XC4+XF1)	C30/37	0.50	320	x
Czech Republic	XC1 to XC4 or XF1	C30/37	0.50 or 0.55	300	x
Denmark	(XC2, XC3, XC4, XF1, XA1)	C25/30	0.55	$150^{3)}$	$(x)^{4)}$
Finland	XC3 or XC4, XF1	C25/30	0.60	$250^{5)}$	x
Germany	XC4 + XF1	C25/30	0.60	280	x
Ireland	XC2 or XC4 + XF1	C30/37 if XC4 + XF1	0.55	320	x
Italy	XC1	C25/30	0.60	300	x
	XC2 + XF1	C32/40	0.50	320	x
Luxembourg	XC4 + XF1	C25/30	0.60	280	x
Netherlands	XC3	–	0.55	280	x
	XC4 + XF1	–	0.50	300	x
Norway	XC4 + XF1	–	0.60	250	x
Portugal	XC4 + $XF1^{11)}$	C30/37	0.60	280	x
			0.55	300	x
Slovenia	XC4 + XF1	n. i. a.	n. i. a.	n. i. a.	x
Sweden	XC4, XF1	–	0.55	300	$x^{4)}$
Switzerland	XC4 + XF1	–	0.50	300	x
United Kingdom	XC3/4 + XF1	C28/35	0.60	280	x

x	allowed
(x)	allowed with restrictions
	not mentioned
o	not allowed
n. i. a.	no information available
1)	Due to the complexity of the national annexes, this compilation makes no claim to completeness or to exact reproduction of all specifications.
2)	Cements need testing

stantiated. A drop in the elastic modulus indicates internal damage of the concrete structure. The regulatory code from the BAW (Federal Waterways Engineering and Research Institute) [12] even specifies a limit. According to the BAW regulations concretes have a high freeze-thaw resistance, i.e. are suitable for exposure class XF3, if the drop in elastic modulus after 28 freeze-thaw cycles is no more than 25 %.

In this situation the concretes made with Portland-composite cements also exhibit behaviour like that of the Portland or blastfurnace cements that have been used successfully in these applications for decades (Fig. 7, right).

For the higher levels of limestone it is of interest to find whether the nature of the limestone can influence the result of the laboratory tests. ❱ Table 3 shows the characteristic values of seven limestone meals with a bandwidth of the $CaCO_3$ content between 83 and 98 wt.%. All the limestones fulfilled the requirements of the DIN EN 197-1 cement standard. The BET surface areas of the limestone meals were also determined as additional characteristic values. In this case the bandwidth lay between about 12 000 and about 74 000 cm^2/g. As a supplement to the determination of the standard parameters, namely $CaCO_3$ content, TOC content and methylene blue value, measurement of the BET surface area can be appropriate as a measure of the degree of contamination of the limestone by secondary constituents. The relationship between the specific clay mineral fraction and the BET surface area is known from earlier investigations [13, 14]. The limestone meals were used to produce Portland-limestone cements of the 32,5 R strength class with a limestone content of 35 wt.%, the main properties of which are also given in Table 3.

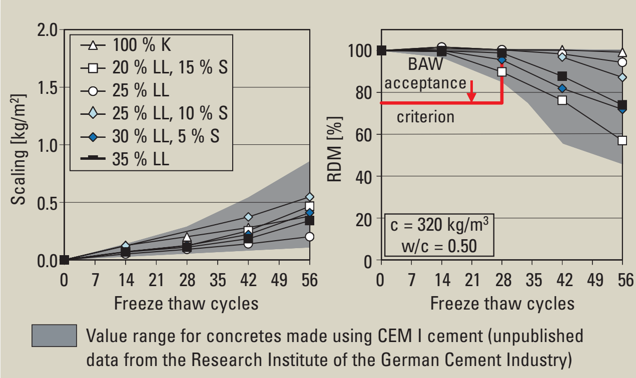

Figure 7: Scaling loss (left) and relative dynamic elastic modulus RDM (right) of concretes made using Portland cement and Portland-limestone cements as well as various Portland-composite cements – CIF test

to DIN EN 206-1 in conjunction with various national annexes – Example: External component with no significant exposure to chlorides (Sources: [2, 3, 4])1)

CEM II																	CEM III			CEM IV		CEM V	
S		D	P/Q		V		W		T		LL		L		M								
A	B	A	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	C	A	B	A	B
x	x	x			x	x	(x)2)						x	(x)2)		(x)2)	x	(x)2)					
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x				
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					
					(x)4)	(x)4)					(x)4)			(x)4)									
x	(x)6)	x			x	(x)6)					x6)				x	(x)6)							
x	x	x	x	x	x	x	o	o	x	x	x	x	o	o	(x)7)	(x)7)	x	x	o	o	(x)8)	(x)9)	(x)9)
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
x	x	x		x					x		x				(x)10)		x	x					
x	x				x	x			x	x							x	x					
x	x				x	x			x	x							x	x					
x		x			x						x		x										
x		x	x		x		x		x		x		x		x								
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	(x)12)			(x)12)	(x)12)	(x)12)	
x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
x4)		x4)			x4)						x4)				(x)4)		x3)	x3)					
x		x									x				(x)4, 13)								
x	x	x		x	x						x	x	x	x			x	x					

3) min filler: 375 kg/m^3

4) Minimum strength class 42,5

5) min c = 270 kg/m^3 for XC4

6) Cement not approved for XC4

7) Only CEM II/A-M (S-D; S-T; S-LL; D-T; D-LL; T-LL; S-P; S-V; D-P; D-V; P-V; P-T; P-LL; V-T; V-LL) and CEM II/B-M (S-D; S-T; D-T; S-P; D-P; P-T; S-V; D-V; P-V; V-T)

8) Only CEM IV/B (P) and valid only for trass complying with DIN 51043, used as a main constituent up to a maximum content of 40 % (m/m)

9) Only CEM V/A (S-P) and CEM V/B (S-P) and valid only for trass complying with DIN 51043

10) Only CEM II/A-M (S-D; S-T; S-LL; S-V)

11) Assumption

12) Not less than 50 wt.% clinker

13) Only CEM II/A-M (D-LL)

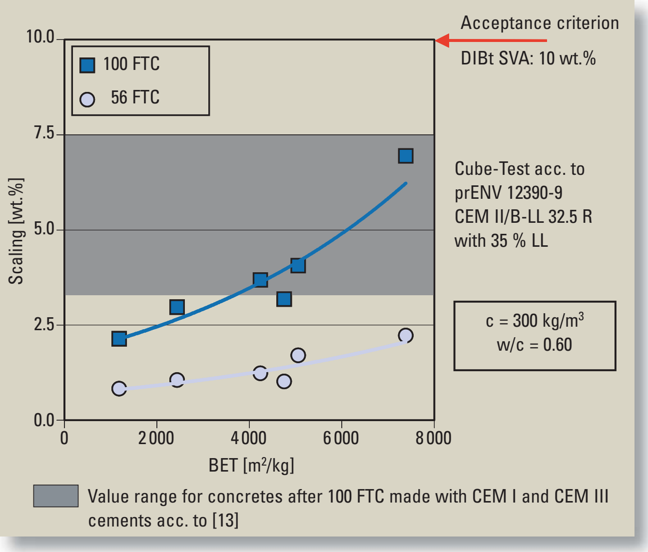

Figure 8: Scaling loss of concretes made using Portland-limestone cements containing 35 wt.% limestone in the cube test, as a function of the BET surface area of the limestone meal

❯ Fig. 8 shows the scaling losses of concretes, determined by the cube method specified in prEN 12390-9:2002 using Portland-limestone cements with a limestone content of 35 wt.%, as a function of the BET surface area of the limestone meal. The cube test – when applied to concretes with a water/cement ratio of 0.60 – is also used in the approval tests of the DIBt (German Institute for Building Technology) and is therefore a prominent evaluation criterion. In general, there is a good correlation between the scaling losses determined by the cube test and the concrete compressive strengths obtained from the limit values for the concrete composition in DIN 1045-2 (cf. e.g. [6]). Cements that have been positively assessed in the approval tests using this assessment criterion have also proved successful in practice. The type of limestone has no known influence with limestone contents up to about 25 wt.% [13]. However, at higher levels of limestone there is a relationship between the weathering losses in the laboratory test and the degree of contamination of the limestone by secondary constituents, characterized by the BET surface area of the limestone component. For the purposes of classification Fig. 8 also contains the value range for scaling losses after 100 freeze-thaw cycles for concretes made with Portland cement and blastfurnace cements taken from investigations by the Research Institute as well as the limit of 10 wt.% used for the approval investigations by the DIBt. As the degree of contamination of the limestone by secondary constituents increases the scaling losses of the concrete after 100 freeze-thaw cycles approaches the upper boundary of the value range and the actual limit. If cements containing higher levels of limestone are to be approved for concretes exposed to frost then, if applicable, an additional requirement for the limestone quality should be formulated.

4.6 Resistance to freeze-thaw with de-icing salt

Concretes made with Portland-composite cements containing up to 35 wt.% granulated blastfurnace slag and limestone can also exhibit high resistance to freeze-thaw with de-icing salt. The performance of the concretes made using Portland-composite cements were checked here by freeze-thaw tests with de-icing salt using the CDF test (❯ Fig. 9). In this test a scaling loss of 1500 g/m² after 28 freeze-thaw cycles is normally used as the acceptance criterion for concretes that have a high resistance to freeze-thaw with de-icing salt. If this acceptance criterion is applied to concretes with artificially introduced air voids for the XF4 exposure class with Portland-composite cements then it can be seen that concretes made using Portland-limestone cements with 35 wt.% limestone have very low scaling losses (Fig. 9, left). This does not change even when the test is continued up to 56 freeze-thaw cycles.

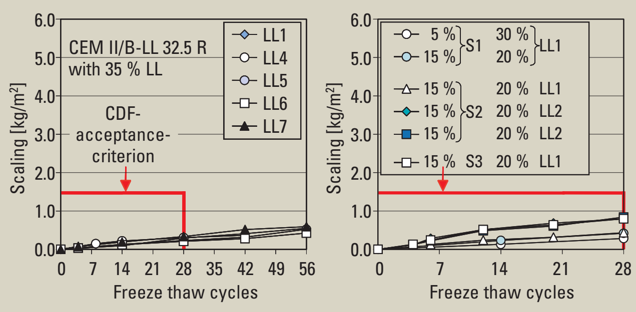

Figure 9: Scaling loss of air-entrained concretes with w/c = 0.50 and c = 320 kg/m³ made using Portland-limestone cements (left) and various CEM II/B-M (S-LL) 32,5 R Portland-composite cements (right) in the CDF-Test

The right-hand side of Fig. 9 shows the scaling losses of concretes made with different Portland-composite cements that were produced using Portland cement clinker in combination with three granulated blastfurnace slags and two different limestone materials. For capacity reasons the trials were only carried out up to 28 freeze-thaw cycles. The scaling losses of the concretes remained significantly below the acceptance criterion of 1500 g/m² after 28 freeze-thaw cycles. This means that the concretes have a high resistance to freeze-thaw with de-icing salt and can be used in the XF4 exposure class. As with the investigations of the freeze-thaw resistance (see Section 4.5) it is not possible to differentiate here between the individual results on the basis of the respective cement compositions.

Table 3: Properties of limestone meals and CEM II/B-LL Portland-limestone cements

Parameter/Limestone			LL						
			1	2	3	4	5	6	7
$CaCO_3$		wt.%	98.6	91.6	96.6	93.2	83.1	83.7	87.7
TOC			0.013	0.074	0.013	0.081	0.081	0.067	0.093
Methylenblue value		g/100 g	0.03	0.40	0.13	0.27	0.33	0.23	0.33
Blaine value		cm²/g	7000	10000	7000	5400	5450	5150	4400
BET value			11880	50590	24360	65780	42410	47510	73810
CEM II/B with 35 % LL (fineness of clinker + sulfate agent: 5200 cm²/g)									
Water demand		M.-%	30.5	33.5	30.5	31.0	31.0	32.0	32.5
Compressive strength	2 d	MPa	32.5	35.5	33.4	31.8	32.0	32.8	31.7
	28 d		47.0	52.5	46.6	46.9	46.5	48.0	46.5

5 Conclusions and outlook

The production and use of cements with several main constituents and reduced levels of clinker make a substantial contribution to climate protection. Cements with several main constituents also prove to be viable alternatives to Portland cements from the technical point of view. CEM II-M Portland-composite cements provide a special opportunity to develop these cements further into even more robust systems by combining several main constituents. This is most effective with combinations of limestone and granulated blastfurnace slag. This has been demonstrated using the examples of carbonation, resistance to chloride penetration and the resistance of concrete to freeze-thaw and to freeze-thaw with de-icing salt. CEM II-M cements are primarily used for industrial purposes in Germany as CEM II/B-M (S-LL) cements, with Portland cement clinker, granulated blastfurnace slag and limestone as the main constituents. Similar results can be expected from the combination of limestone and coal fly ash complying with EN 450 as main cement constituents.

With further increasing quantities of granulated blastfurnace slag CEM III/A cements containing up to 50 wt.% granulated blastfurnace slag will also become increasingly important in Germany in the future as robust universal cements in building construction and civil engineering.

Future investigations at the Research Institute of the Cement Industry will also, for example, deal with CEM IV and CEM V cements, which until now have been largely unknown in Germany, in order to determine the potential strength development and durability of the concretes produced with them. ◂

LITERATURE / LITERATUR

[1] Zahlen und Daten 2004-2005. Bundesverband der Deutschen Zementindustrie.
[2] Survey of national provisions. Final draftrev2 (Document CEN/TC 104 N0687). 13 October 2005 – not published.
[3] DIN 1045-2: Concrete, reinforced and prestressed concrete structures. Part 2: Concrete – Specification, properties, production and conformity – Application rules for DIN EN 206-1.
[4] European Construction in Service of Society (ECOServe) – Cluster 2: Production and application of blended cements (www.eco-serve.net/publish/cat_index_16.shtml).
[5] Kühn, A.; Lang, E.; Müller, C.; Schnedl, G.: Cements with several main constituents – A durable solution. Presentation given at VDZ Seminar „Cement chemistry“, Düsseldorf, April 2005.
[6] Müller, C.; Lang, E.: Durability of concrete made with Portland-limestone and Portland-composite cements CEM II-M (S-LL). beton 55 (2005), No. 3, pp. 131–138; No. 4, pp. 197–202; No. 5, pp. 266–269 (in German).
[7] Schießl, P.; Meng, B.: Neuer Ansatz zur Charakterisierung der Porenstruktur zementgebundener Baustoffe im Hinblick auf die Interpretation von Transportvorgängen. Aachen: Institut für Bauforschung, 1998. – Forschungsbericht Nr. F 526.
[8] Manns, W.; Thielen, G.; Laskowski, C.: Bewertung der Ergebnisse von Prüfungen zur bauaufsichtlichen Zulassung von Portlandkalksteinzementen. beton 48 (1998), No. 12, pp. 779–784.
[9] Stark, J.; Wicht, B.: Dauerhaftigkeit von Beton. – Weimar: Hochschule für Architektur u. Bauwesen Weimar, 1995. – (Hochschule für Architektur u. Bauwesen Weimar, Schriften 100). – ISBN 3-86068-041-2.
[10] Brodersen, H. A.: Transportvorgänge verschiedener Ionen im Beton. Beton-Informationen 23 (1983), H. 3, pp. 36–38.
[11] Deutscher Ausschuss für Stahlbeton; DAfStb: Richtlinie Massige Bauteile aus Beton, Ausgabe März 2005.
[12] Bundesanstalt für Wasserbau (BAW): Merkblatt „Frostprüfung von Beton“ – Ausgabe Dezember 2004
[13] Siebel, E.; Sprung, S.: Einfluss des Kalksteins im Portlandkalksteinzement auf die Dauerhaftigkeit von Beton. In: Beton 41 (1991), Nr. 3, S. 113–117; Nr. 4, S. 185–188
[14] Sprung, S.; Siebel, E.: Assessment of the suitability of limestone for producing portland limestone cement (PKZ). In: Zement-Kalk-Gips 44 (1991), Nr. 1, S. 1–11
[15] (Norm-Entwurf) DIN EN 12390-9, Ausgabe:2002-05. Prüfung von Festbeton – Teil 9: Frost- und Frost-Tausalzwiderstand; Abwitterung; Deutsche Fassung prEN 12390-9:2002.