



**EUROPEAN CONSTRUCTION IN SERVICE OF SOCIETY
ECOserve NETWORK**

**CLUSTER 2
Production and Application of Blended Cements**

Network Activities

Blended cements

*The sustainable solution for the cement and concrete
industry in Europe*

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0 Imprint

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1 Introduction

1.1 General

The cement production process is intensive in energy as well as in raw material demand. Limits of technical improvements to lower the environmental impact of the cement production have been reached in the European cement industry. Remaining potential to reduce environmental impacts is provided by the reduction of the clinker content in cement (blended cements). Other main constituents for cement like granulated blastfurnace slag (gbs), fly ashes from power plants, natural and industrial pozzolanas or limestone can be used. The production of blended cements results in lower emission and lower energy consumption since less clinker from the energy-intensive process is needed to produce such blended cements.

Essentially, national and European cement standards allow the partial replacement of cement clinker by other substances. Of particular significance throughout the world are granulated slag from the production of pig iron, fly ash and uncalcined limestone. In addition, regionally there is a growing number of mineral substances which are coming into use as cement minor constituents. In the evaluation of the potential represented by these, the different properties and the performance of the cement types produced from them have to be taken into account. The degree of substitution can be characterised by the clinker-cement factor. The lower the clinker-cement factor, the higher is the degree of substitution of the clinker by other main cement constituents. In Germany, as an example, the average clinker-cement factor is at present 0.78 [Hoe03]. **Figure 1** shows the effect of the substitution of clinker by granulated slag for a CEM II/B-S 32.5 with 35 % granulated slag. The calculations are based on an average fuel energy consumption of 3500 MJ/t clinker, the use of hard coal as fuel and a CO₂ emission factor for electricity generation of 0.67 t CO₂/MWh, typical for Germany. Under these conditions, the production of one tonne of Portland cement, which was produced using 5 % sulphates and 5 % minor additional constituents is associated with a total CO₂ emission (including that for the electricity) of 0.842 t CO₂/t cement. As a result of clinker substitution with 35 % granulated slag, a reduction in the specific fuel-derived CO₂ emissions of approx. 0.09 t CO₂/t would be attained. Additional thermal energy is, however, necessary for the drying of the granulated slag (ca. 0.02 t CO₂/t cement) and if necessary for the transport from the steel works to the cement works (not taken into account here). The effect of the electricity-related CO₂ emissions is also negligible, given the relatively high German emission factor for electricity generation. Power saving by clinker substitution and higher power consumption because of the finer grinding of the CEM-II cement balance one another out. By far the greatest saving effect is produced by

the reduction of the raw material-related CO₂ emissions from the limestone, with just 0.15 t CO₂/ t cement. In total, a reduction of approx. 0.22 t CO₂/ t cement or 26 % is obtained.

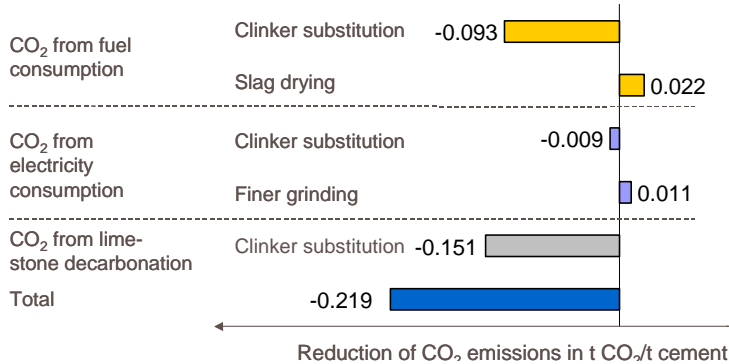


Figure 1: CO₂ reduction from the production of blended cements in Germany [Hoe03] – revised data

Figure 2 below shows the raw material-related and energy-related CO₂ emissions in the production of composite cements as a function of the content of other main cement constituents. The calculations are based on the same boundary conditions as stated previously. The diagram applies for cements of the strength class 32.5 N/mm². It is clear that the CO₂ emission decreases approximately linearly with the content of the other main constituents. Based on the energy-related specific CO₂ emissions, a saving of approx. 54 % can be achieved by an 80 % replacement of the clinker with ground granulated slag. The main reasons for this are the need to dry the granulated slag and the need for finer grinding of the CEM III cement. On the other hand, if the raw material-derived CO₂ emissions are also included, the possible saving is 72 %.

Technical improvements and the consistent shift of the cement portfolio to blended cements leads to the reduction of the mean specific CO₂ emissions per ton of cement. An example for a Greek cement producer is given in **Figure 3**.

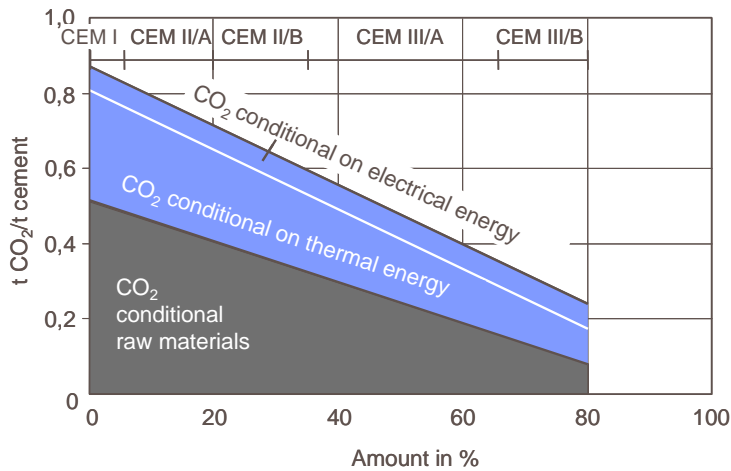


Figure 2: CO₂ emissions from the production of blended cements in Germany [Hoe03]

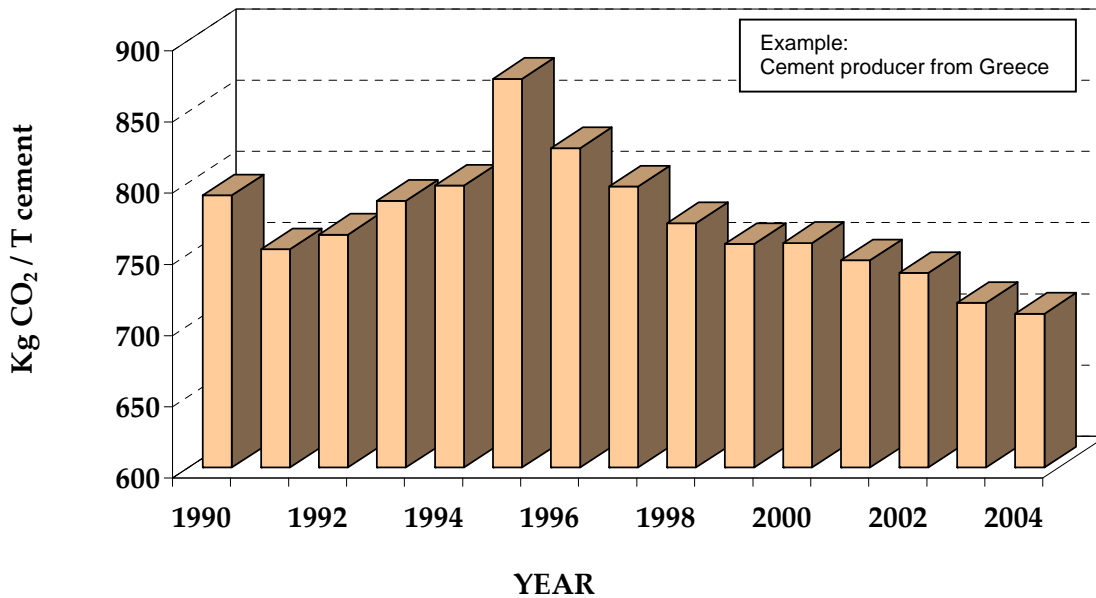


Figure 3: Example for the development of CO₂ emissions per ton of cement for one cement producer (period 1990-2004)

CO₂ is generated from three independent sources: de-carbonation of limestone in the kiln (about 525 kg CO₂ per tonne of clinker), combustion of fuel in the kiln (about 335 kg CO₂ per tonne of cement) and use of electricity (about 50 kg CO₂ per tonne of cement). It should be noted that this latter is not covered by the Emissions Trading Directive which only intends to cap direct emissions [Cem06].

In 2003 the cement industry in the European Union produced about 194 million tonnes of cement and emitted about 0.75 tonne of CO₂ per tonne of cement via direct emissions (fuel combustion and raw material de-carbonation) and 0.05 tonne of CO₂ per tonne of cement via indirect emissions (use of electricity from fuel based power plants). Direct and indirect emissions of CO₂ together amounted to about 0.8 tonne of CO₂ per tonne of cement [Cem06].

There are three measures by which the cement industry may save direct CO₂ emissions in the immediate future [Cem06]:

- Improvement of energy efficiency (a maximum of 2% is still feasible),
- **Reduction of clinker/cement ratio** (introduction of useful industrial by-products),
- Increase in the use of waste as alternative fuel (national initiatives, adequate national implementation of certain directives regarding specific waste). Certain fuels may qualify for the term / category CO₂-neutral: This applies to fuel types substituting fossil fuel, e. g. bioenergy (CO₂ bound through “production”) or waste (alternative handling would lead to equivalent or higher environmental consequences). Hence, the application of such fuels are considered advantageously concerning stabilization of the climatic balance.

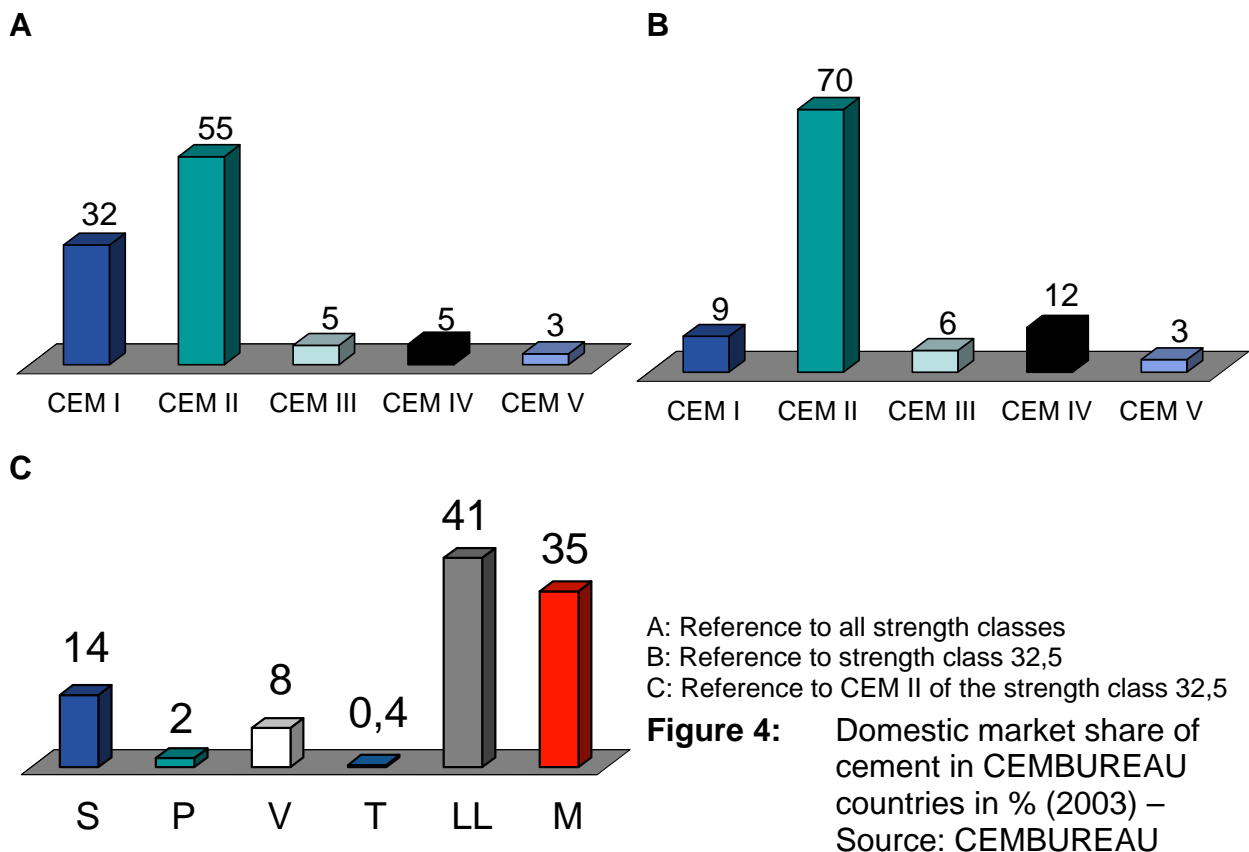
The cement industry contributes to about 3% of the total anthropogenic emissions of CO₂ in the European Union [Cem06].

1.2 Blended cements in Europe

A wide variety of common cement products exist in the different EU Member States. They match local manufacturing conditions, throughout meeting particular climatic or other local conditions, including building practices. The industry has identified and agreed upon 27 common cement products, which are standardized in the European cement standard EN 197-1. The standard defines these 27 common cement products and their constituents. It includes specifications on the proportions in which they are to be combined, as well as the mechanical, physical and chemical requirements for both the products and their constituents. The products are divided into 5 groups, according to the content of constituents other than cement clinker. Since April 2002, all common cements have been CE-marked according to EN 197-2. Besides Portland cement CEM I all other cements are blended cements (**Table A1**).

Ecological and economical reasons initiated a change in the development of different types of cement throughout Europe. CEM I cements are being increasingly replaced by

CEM II cements which contain other main constituents in addition to clinker. **Figure 4** gives a survey of the European cement sales for the year 2003 according to CEMBUREAU statistics. Portland cement continues to play the dominant role in the 52,5 strength class, but in the 32,5 and 42,5 cement strength classes there have been substantial moves towards CEM II cements. Overall the amount of Portland cement in the CEMBUREAU countries in the year 2003 represent 32 %, whereas the amount of blended cements was about 64 % (**Figure 4A**). In the strength class 32,5 the amount of Portland cement in the CEMBUREAU countries in the year 2003 represent only 10 %, whereas the amount of blended cements was about 90 % (**Figure 4B**). Unspecified cements are not shown in the figures.

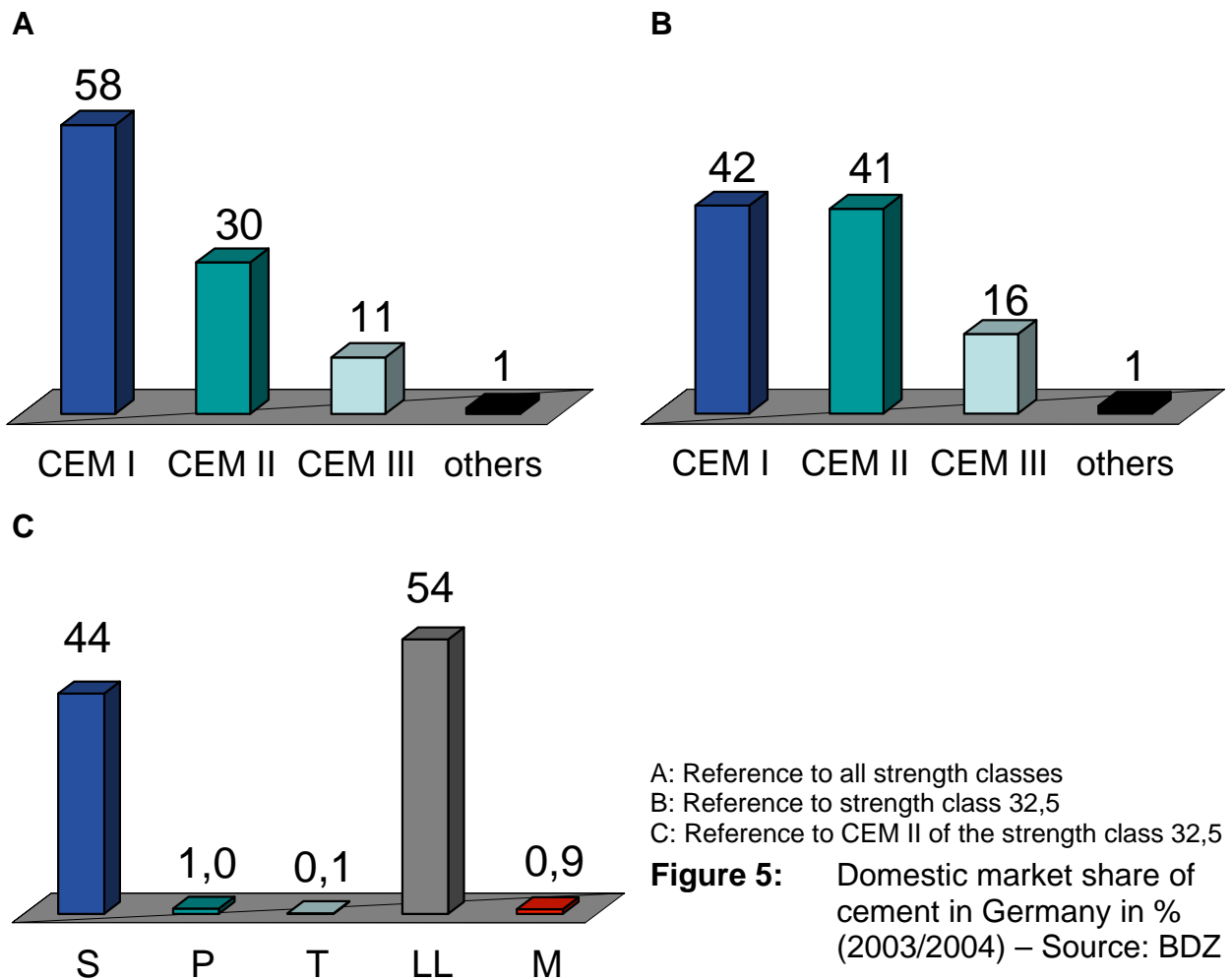


Portland limestone cements are most frequently used as Portland-composite cement CEM II, followed in second place by Portland-composite cements CEM II-M with more than two main constituents (**Figure 4C**). CEM II-M cements have shown the greatest increase in recent years. However there are partly considerable differences regarding cement types in various European countries. Besides regional selling conditions this

also has to be attributed to restrictions in view of the application of some of the Portland-composite cements and blended cements respectively. Following examples are given in comparison to the pan-European situation:

Example: Domestic market share Germany

Figure 5 gives a survey of the German cement sales for the years 2003 and 2004 according to statistics of the German Cement Association (BDZ). Overall the amount of Portland cement in Germany in the year 2003 represent 58 %, whereas the amount of cements with several main constituents was about 42 % (**Figure 5A**). In the strength class 32,5 the amount of Portland cement in Germany in the year 2003 represent 42 %, whereas the amount of cements with several main constituents was about 58 % (**Figure 5B**).



Unspecified cements are not shown in the figures. In 2004 Portland limestone cements were most frequently used as Portland-composite cement CEM II, followed in second place by Portland-slag cements CEM II-S (**Figure 5C**).

Example: Domestic market share Greece

The domestic deliveries in Greece during 2004 were dominated by blended cements as their quantity covered approximately 90% of the total cement production (**Figure 6**). The production of CEM I was representing ~ 25 – 27 % of the cement market in the early nineties, after 1993 its market share was shrinking and by 2004 it was almost totally replaced by blended cements.

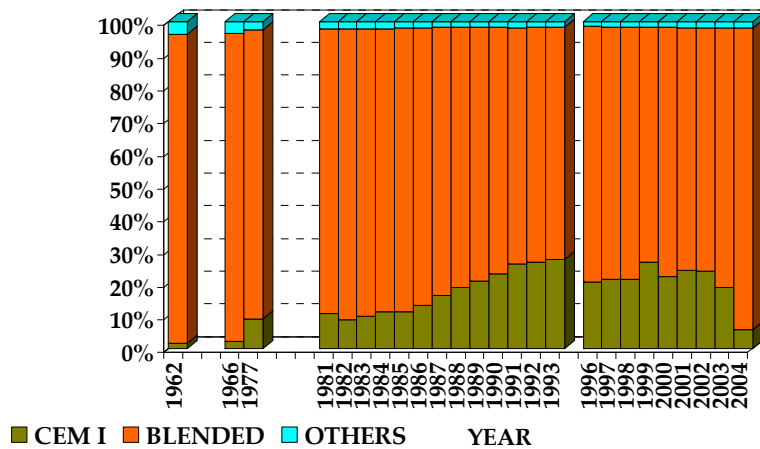


Figure 6: Domestic market share Greece – Source: Titan Cement

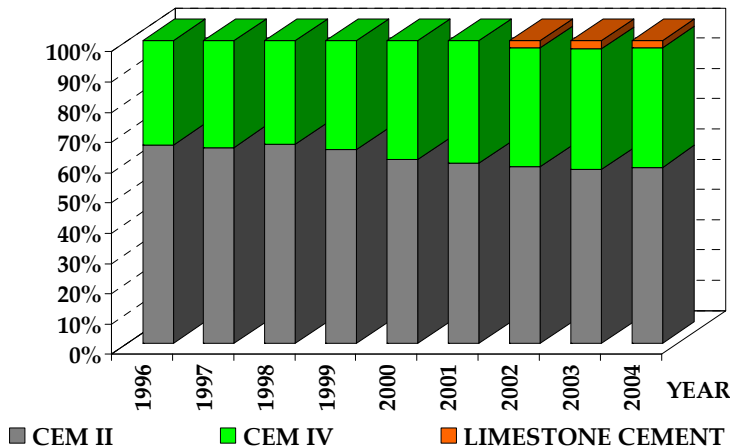


Figure 7: Blended cements market share in Greece – Source: Titan Cement

Two types of blended cements are currently produced in Greece, CEM II and IV with different combinations of main constituents. In detail CEM II dominates the market of blended cements with almost double share compared to CEM IV (**Figure 7**).

Example: Domestic market share Italy

Figure 8 shows the Italian cement production (import which accounts for about 5% is excluded) for year 2004 according to statistics of Italian Technical Economical Association of Cement (AITEC). The total amount of cement other than CEM I is higher than 90 %. The most important cement type is CEM II with a production share of more than 75 %.

The total production share of limestone cement with respect to CEM II type cement is higher than 80 % (**Figure 9**).

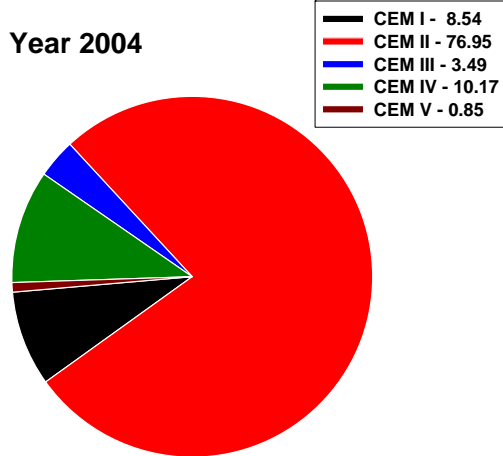


Figure 8: Domestic market share Italy – Source: AITEC

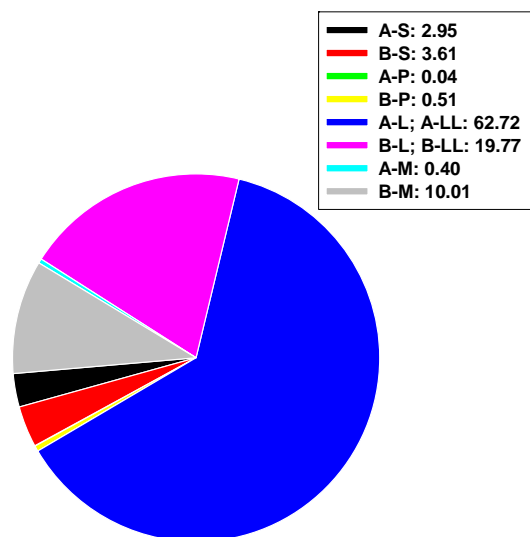


Figure 9: Blended cements market share in Italy – Source: AITEC

With respect to strength classes it has been observed a clear trend of increase of higher strength classes and corresponding decrease of lower strength class. In **Figure 10** the production shares are shown.

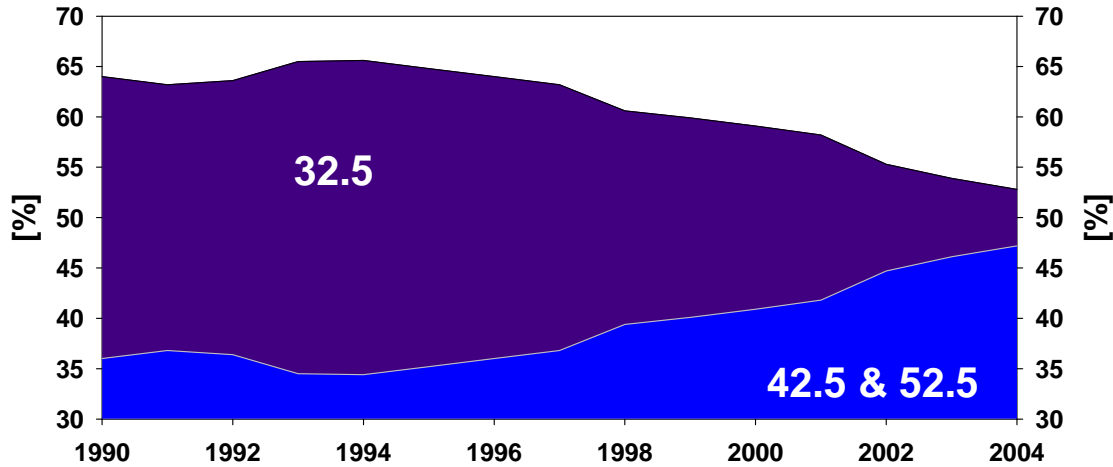


Figure 10: Market share with regard to stand strength of cement in Italy – Source: AITEC

Example: Domestic market share in Poland

The market in Poland in 2004 was supplied with about 30 types of cement. In the total volume of cement produced, 43.5 % was Portland cement CEM I, 48.6 % were Portland-composite cements CEM II, and 7.7 % were Blastfurnace cements CEM III (**Figures 11 and 12**).

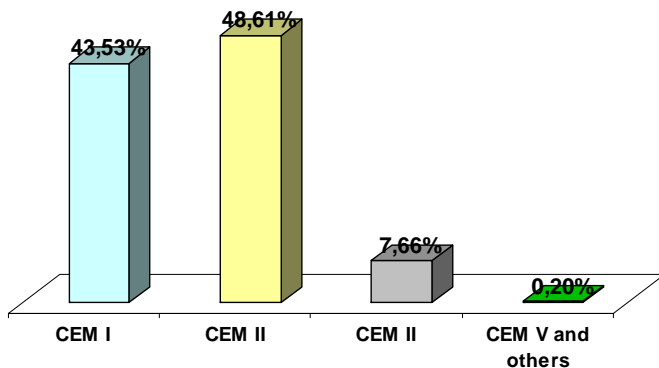


Figure 11: The market share of cement in Poland in 2004 (in reference all strength classes) – Source:

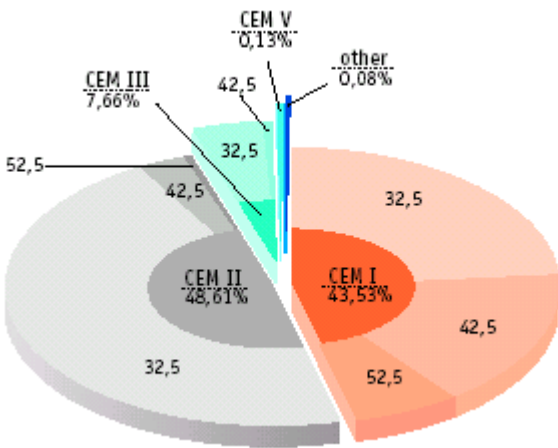


Figure 12: The market share of cement in Poland with a partition into strength classes in 2004

Example: Domestic market share in Norway and Sweden

The product mix for Norway and Sweden in 2005 is given in **Figures 13 and 14**.

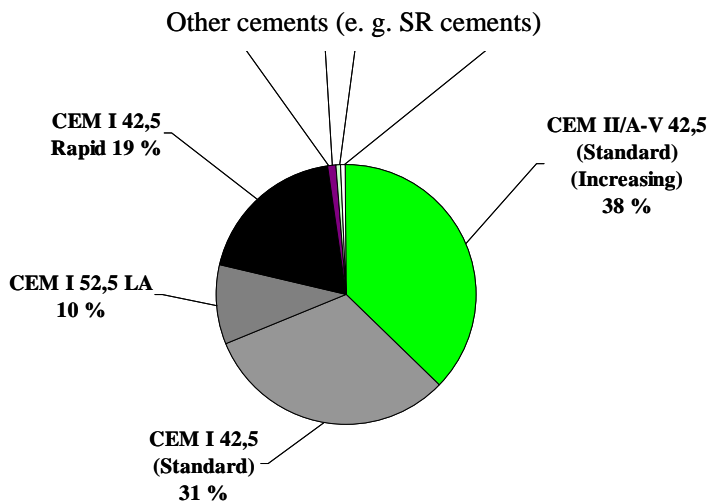


Figure 13: Norway Product Mix – 2005 – Source: NORCEM

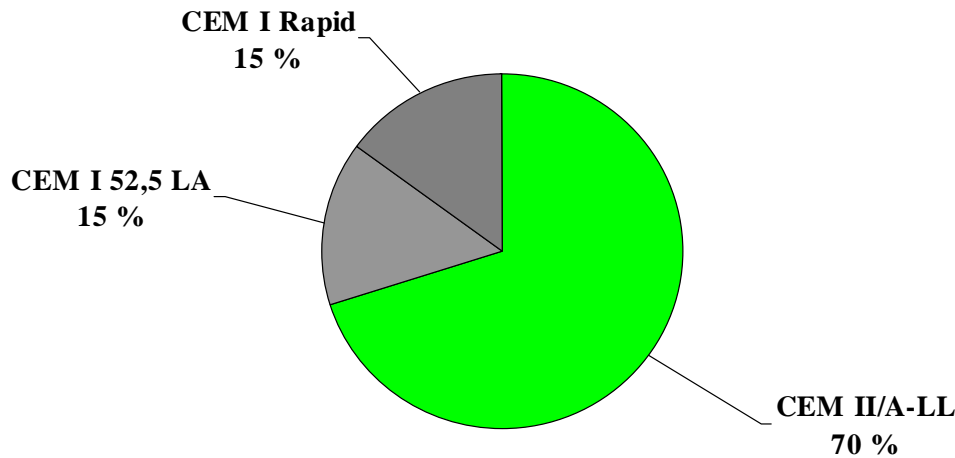


Figure 14: Sweden Product Mix – 2005 – Source: NORCEM

1.3 Application rules for blended cements

Experience in the production and application of blended cements already exists as most of cements produced and/or used in Europe are blended cements (**Figure 4**). 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. 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. The k-value concept for fly ash has been generally applied to blended cement using k-values in the range of 0.2 and 0.5 [Cen06].

2 Performance of blended cements

2.1 Cement

2.1.1 General

A multitude of cement properties is influenced by the cement composition. Amongst others these are:

- Partice size distribution / fineness;
- Setting;
- Water demand;
- Strength development / secondary hardening;
- Heat of Hydration;
- Alkali content;
- Brightness.

The influence of different main constituents besides clinker on these properties will be illustrated subsequently.

2.1.2 Particle size distribution / fineness

Blended cements generally consist of two or three main constituents, and one of the critical adjustable parameters in terms of quality is their particle size distribution. Blended cements generally speaking have a higher fineness than CEM I of the same strength class, a behaviour that can be seen in **Figures 15 and 16**. This can contribute to a better workability especially of concrete with a low amount of fines. The higher fineness of blended cements does not necessarily result in disadvantages with regard to concrete properties. **Figure 15** illustrates some typical Blaine values for CEM I and CEM II in Greece and **Figure 16** the differential particle size distribution for CEM I, CEM II and CEM IV, where the curves of the blended cements are shifted towards finer particles relatively to CEM I curve. In regions where concrete and aggregate business is “small business” (SME enterprises), the fineness of finely ground blended cement or additions may represent challenges and call for a differentiated approach. In such cases however, a blend may also provide the optimized solution to the technical and logistic problem.

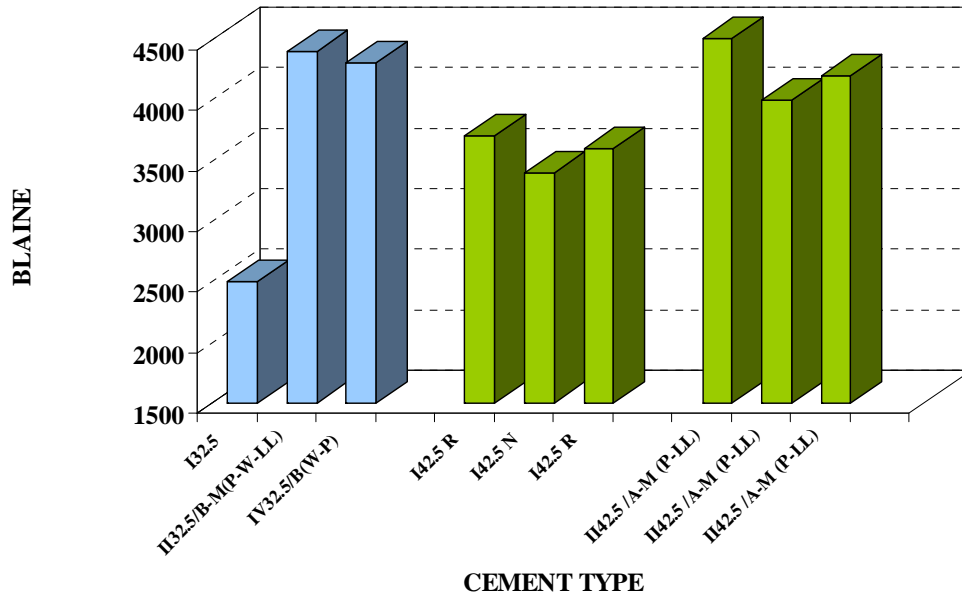


Figure 15: Typical fineness (Blaine values in cm²/g) for CEM I and CEM II in Greece – Source: Titan cement

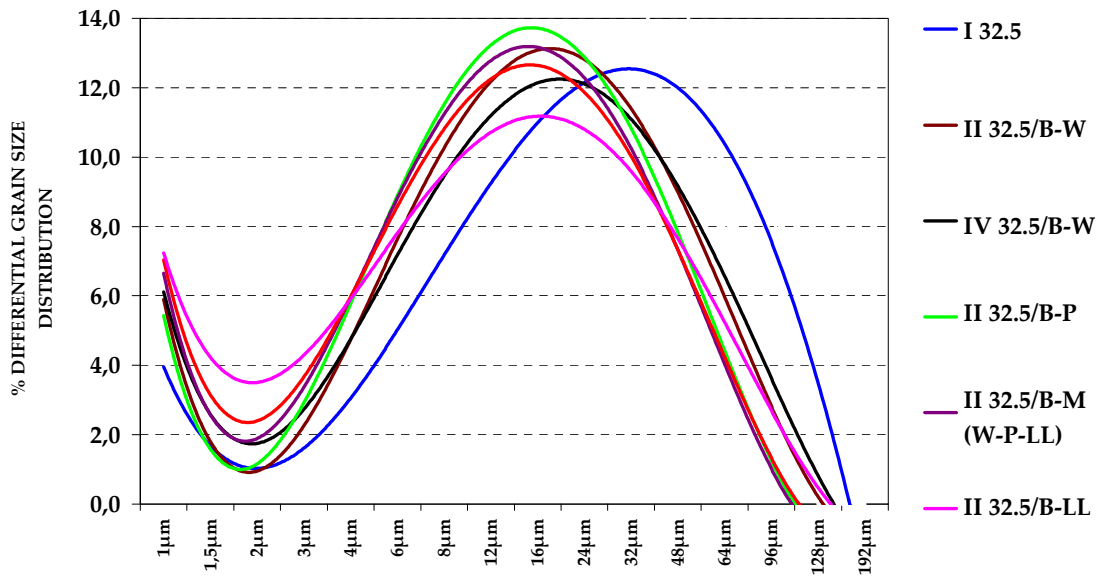


Figure 16: Differential particle size distribution for different blended cements of strength class 32,5 in Greece – Source: Titan cement

2.1.3 Setting

Blended cements generally tend to have increased setting times with an increasing content of main constituents besides clinker. E. g. the fineness of limestone cements is higher than the corresponding CEM I cement in the same strength class. This may therefore result in a decreased setting time when the accelerating effect of finer clinker is prevailing over the retarding effect due to the lower clinker content.

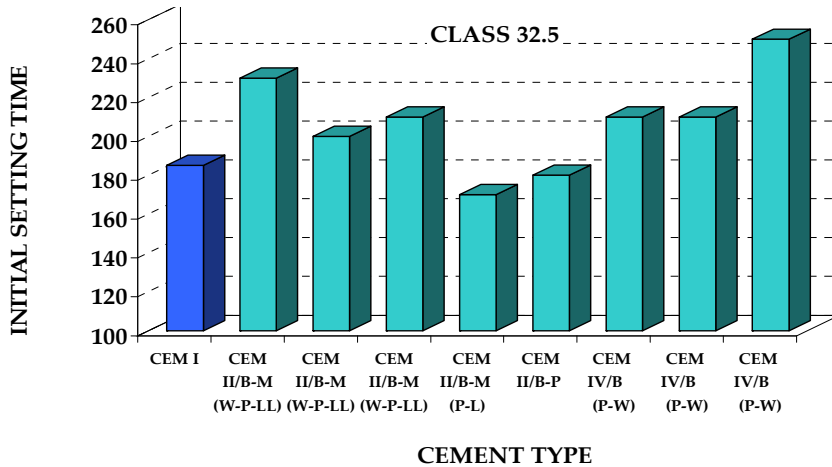


Figure 17: Initial setting of different greek cements of strength class 32,5 – Source: Titan cement

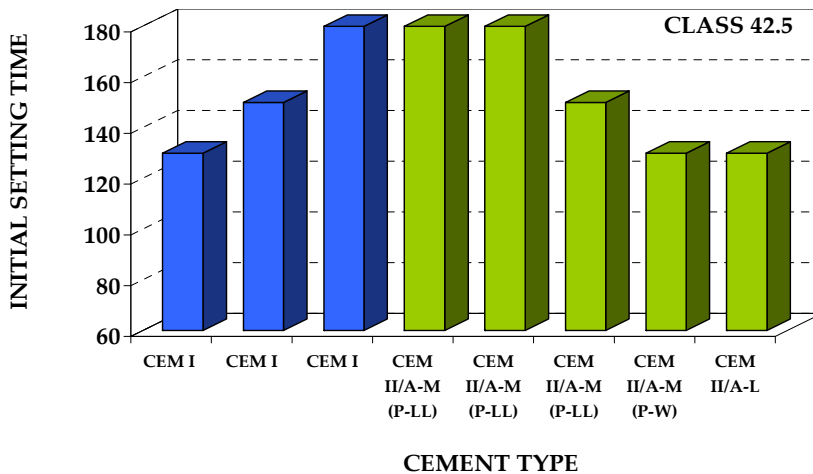


Figure 18: Initial setting of different greek cements of strength class 32,5 – Source: Titan cement

The temperature effect on setting will be enhanced, but the effect may be more predictable with a certified, blended cement compared to the use of combinations of additions and CEM I (or others). Nevertheless, adjustment of setting is not an issue since the control of gypsum addition (just like for CEM I) will determine the setting and will satisfy the market demand (**Figures 17 and 18**). Blended cements in general are beneficial because less retarder (admixture) is needed. A possible mechanism for acceleration is the formation of new nucleation sites for calcium hydroxide [Sor76]. Calcium carbonate additions also influence the C_3S hydration being incorporated in C-S-H structure [Ram86a].

2.1.4 Water demand / Workability

The water demand (acc. to EN 196-3) of blended cements containing ggbs can be slightly higher than the water demand of Portland cements. Generally there is no direct correlation between the water demand acc. to EN 196-3 and the water demand / the workability of the concrete, because the influence of the cement is superimposed by other influences (e. g. aggregate, grading, admixtures). Nevertheless the resulting particle size distribution of the limestone in interground Portland limestone cements exerts a very beneficial effect on the water demand of the cement [Opo92, Tsi92].

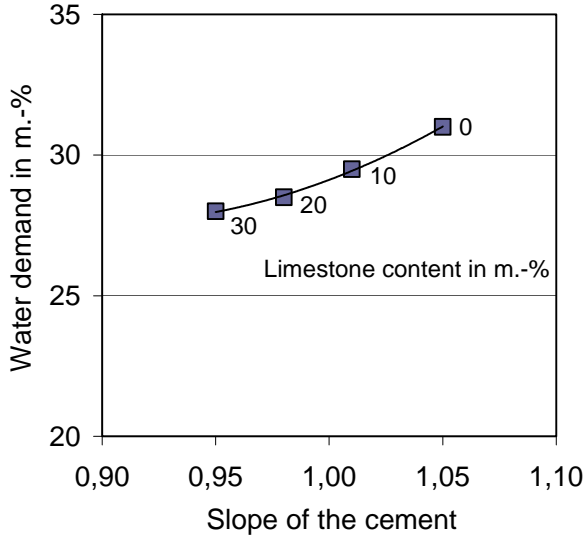


Figure 19: Water demand as a function of the slope and the limestone content in Portland limestone cement [Lud03]

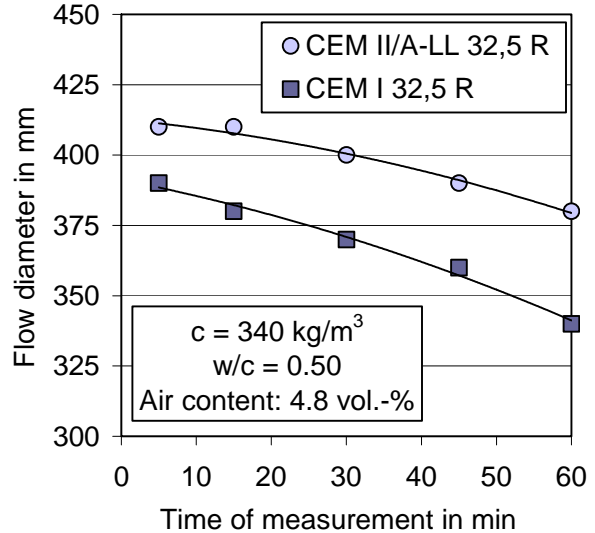


Figure 20: Flow diameter as a function of time and the cement type [Lud03]

Figure 19 shows the water demand as a function of the limestone content for interground cements with the same 28 day compressive strength (approximately 52 N/mm²). In **Figure 19** it can be seen, that the water demand can decrease with increasing limestone content. Although the cements have to be ground finer with increasing amount of limestone the water-depleting influence of the more finely ground clinker fraction is offset by the partial replacement of clinker with limestone. On the other hand, the particle size distribution of the Portland limestone cements in this examples becomes flatter – i. e. has a decreasing slope n of the RRSB function - with rising proportion of limestone. The RRSB function is a frequently used distribution function which can provide an approximation of the S-shaped particle size distribution in a simple logarithmic coordinate system. The RRSB function is described uniquely by the position parameter x' and the slope n (**Figure 21**). The position parameter x' is the particle size x at a cumulative mass distribution of 63.2 mass-%. It therefore characterizes the fineness of the cement. The position parameter x' is smaller the greater the fineness of the cement. The slope n describes the width of the particle size distribution. It is larger the narrower the particle size distribution.

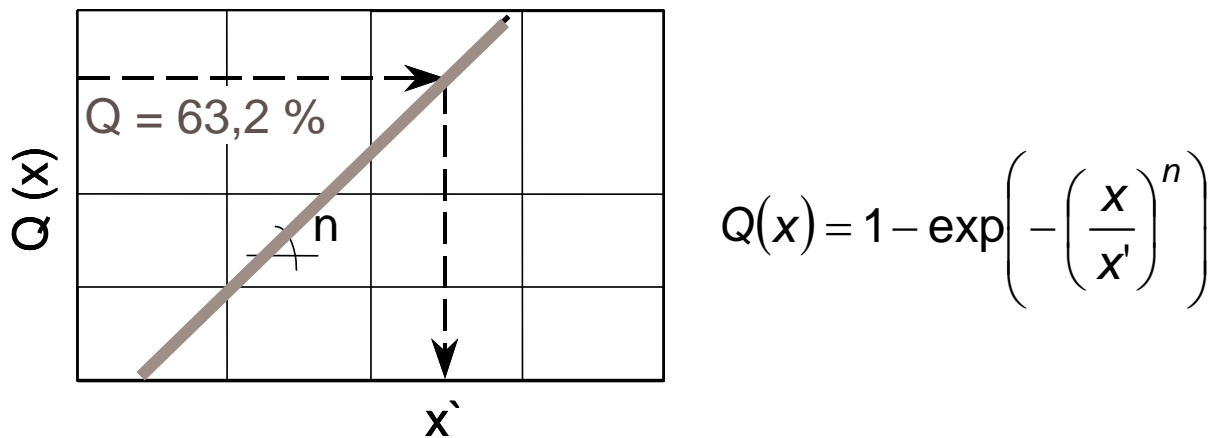


Figure 21: Illustration of the RRSB funktion

As a consequence of the decreasing slope, the water-filled void volume between the ground clinker particles in the cement paste is reduced by filling with fine limestone particles. In practice the two effects can result in a better workability of the concrete. The representation in **Figure 20** contrasts the flow diameter of fresh concrete using Portland limestone cement and Portland cement. It is obvious, that the initial flow diameter rises and the stiffening of the concrete in this example is reduced when Portland limestone cement is used.

2.1.5 Strength development / Secondary hardening

Referring to the same standard compressive strength, the early strength of cements containing gbs, fly ash and natural pozzolana is slightly lower and is decreasing with increasing content of these main constituent. A benefit of cements containing gbs or fly ash is a distinct secondary hardening. Limestone cements do not have any secondary hardening due to pozzolanic activity or latent hydraulic activity of addition (limestone). In any case, as said in 2.1.3, limestone cements are generally characterised by higher fineness and this will generally lead to early strength increase [Bar87].

2.1.6 Heat of hydration

The amount of heat generated is dependent chiefly upon the chemical composition of the cement, with C_3A and C_3S being the compounds primarily responsible for high heat evolution. The contribution of slag to the heat of hydration has been estimated to 250 to 335 J/g, which is about half of that of the Trisiliciumsilicat C_3S and about 30 % of that caused by the Calciumaluminatferrit C_3A . Another technical benefit of blended cements containing gbs therefore is the decrease in the heat of hydration while replacing portland cement clinker. This effect can be useful for e.g. mass concrete. There is a strong correlation between the heat and strength development (**Figure 22**).

$d = 0,6 \text{ m}$ (steel mould), $c = 330 \text{ kg/m}^3$, $w/c = 0,50$, $T_c = T_e = 20 \text{ }^\circ\text{C}$

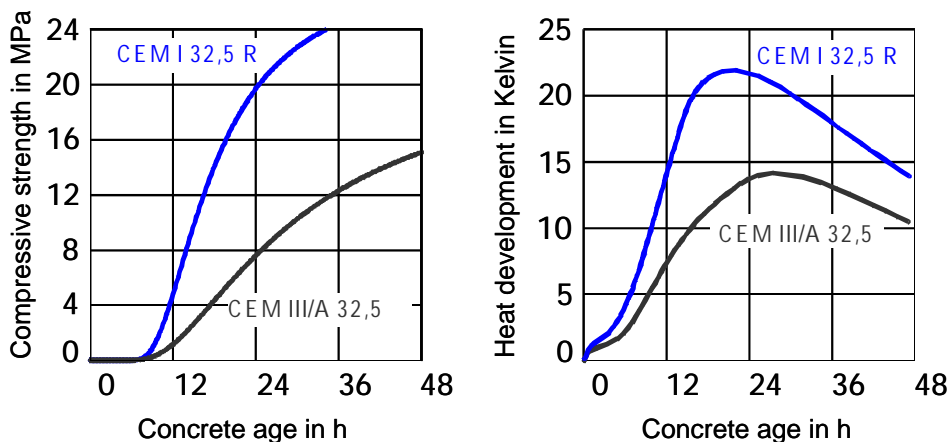


Figure 22: Strength development and heat of hydration of concrete using Portland cement CEM I and Blastfurnace cement CEM III/A – Source: VDZ

Also blended cements containing fly ash have a lower heat of hydration. An example for the heat of hydration of different greek cements of strength class 32,5 is given in **Figure**

23. Low heat common cements recently have been standardized as ammendment A1 to the European cement standard. Blastfurnace cements with a low early strength got their own part as EN 197-4. Special cements with very low heat of hydration – e. g. for mass concrete – have been standardized in EN 14216. These cements with a composition like CEM III/B, CEM III/C, CEM IV/A+B and CEM V/A+B are designated as Very Low Heat Cements VLH with the strength class 22.5 and a heat development less than 220 J/g.

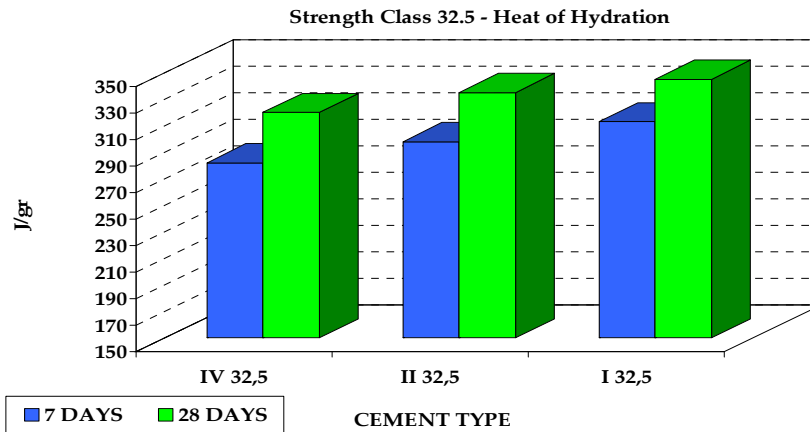


Figure 23: Heat of hydration of different greek cements of strength class 32,5 – Source: Titan cement

The heat of hydration of blended cements containing natural pozzolana is lower than the corresponding CEM I cement. The reduction of the heat of hydration progressively increases with the increase of natural pozzolana content as shown in **Figure 24**.

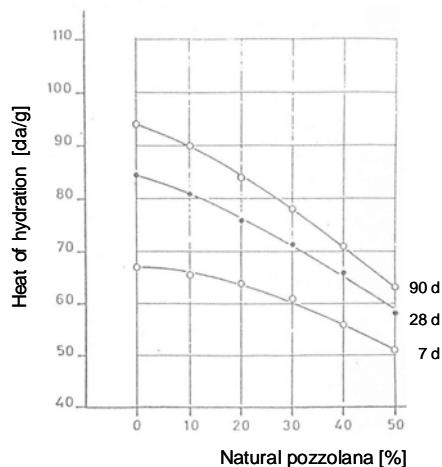


Figure 24: Effect of natural pozzolana content on the heat of hydration at various age – Source: CTG

In cold climates (Northern Europe or inland), the reduced heat generation may demonstrate inconvenient for winter concreting, for which lower blends or special

measures must be applied. A blended cement may exhibit an advantageous, since standard products allow the use of IT tools for modelling and combined industrialized design and performance procedures.

The filler effect consequent to limestone filler addition improves the particle packing of the cementitious system [Eil90] and causes a hydration acceleration of C_3S at early ages [Ram86].

2.1.7 Alkali content

While the effective alkali content of Portland cements rises in line with an increase in the total alkali content, the effective alkali content of cements containing several main constituents may deviate from their total alkali content to varying degrees. This can be traced back to discrepancies in the solubility of the alkalis contained in the cement constituents on the one hand, and to the different alkali absorption by the reaction products on the other hand. Therefore low alkali cements with gbs e. g. in Germany are allowed to have a higher total alkali content dependent on the gbs-content of the cements compared to CEM I low alkali cements.

Regardless of the main constituent used, replacement of the clinker results in a decrease in the alkalinity of the pore solution. The main cement constituents differ significantly in terms of their effectiveness, however. The alkali ion concentration in the hardened cement pastes containing blastfurnace slag does not decrease proportionally to the quantity of clinker replaced, but is reduced less markedly. Part of the alkalis contained in the pore solution thus originates from the blastfurnace slags. Their share is, however, very small in comparison to the clinker. Due to this small share, however, a sizeable decline in the alkali ion concentration cannot be observed until the blastfurnace slag contents exceed 20 wt.%.

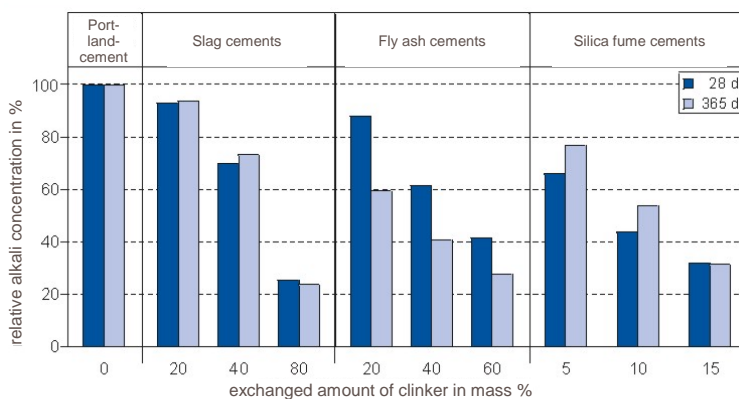


Figure 25: Change in the alkali ion concentration of the pore solution caused by blastfurnace slag, hard coal fly ash and silica fume after different hydration periods [Vdz05]

Up to a hydration time of 28 days, the influence that fly ash utilised in the cement has on the alkalinity of the pore solution is comparable to that of blastfurnace slags. Between 28 and 365 days, however, the alkali ion concentration is reduced substantially. The alkalinity of the pore solution after 365 days is lower than would have been expected on the basis of the reduced clinker quantity alone. A disproportionately high decline in the alkali ion concentration occurs when silica fume is utilised. The replacement of 15 wt.% clinker by silica fume results in a reduction in the alkali ion concentration to approx. 1/3 of the concentration found in the pore solution of the hardened Portland cement paste. As hydration time progresses, however, the alkali ion concentration in the pore solution has been found to increase in all hardened cement pastes containing silica fume [Vdz05].

2.2 Concrete

2.2.1 General

This chapter deals with the influence of blended cements on concrete properties. Concrete durability is centred.

2.2.2 Handling / Setting time

The effect of limestone meal on the water demand of the cement and the workability of concrete was already discussed in chapter 2.1.4. Presumed constant amount of cement and water, concrete using blended cements has a higher cement paste volume due to the lower cement density. This will often have a positive impact on concrete workability and finishing properties, at least for low/normal strength classes and with industrially manufactured/processed aggregates.

2.2.3 Porosity / Pore size distribution / Density

Nearly all concrete properties – especially durability - are influenced by the porosity and the pore size distribution of the cement paste. Both parameters are influenced by different main constituents in a different manner. **Figure 26** shows the influence of cements containing limestone (LL), fly ash (V), silica fume (D) and granulated blastfurnce slag (S) on the total porosity and the pore size distribution of cement paste compared to cement paste with Portland cement. The definition of a relationship between paste porosity and concrete durability requires a case by case assessment.

Whereas higher amounts of limestone meal can lead to a higher porosity and especially to a higher amount of capillary pores $> 0,1 \mu\text{m}$, the use of blended cements containing silica fume or higher amounts of fly ash or granulated blastfurnace slag causes an incerase of fine pores and a decrease of capillary pores resulting in a higher density of the concrete containing these blended cements (**Figure 26**).

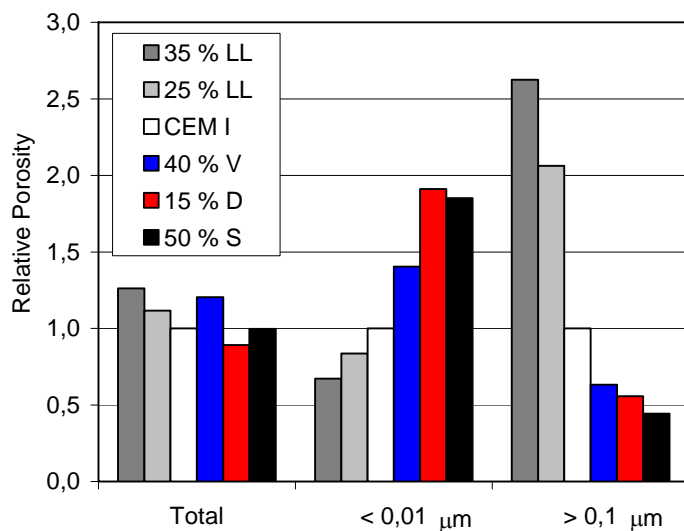
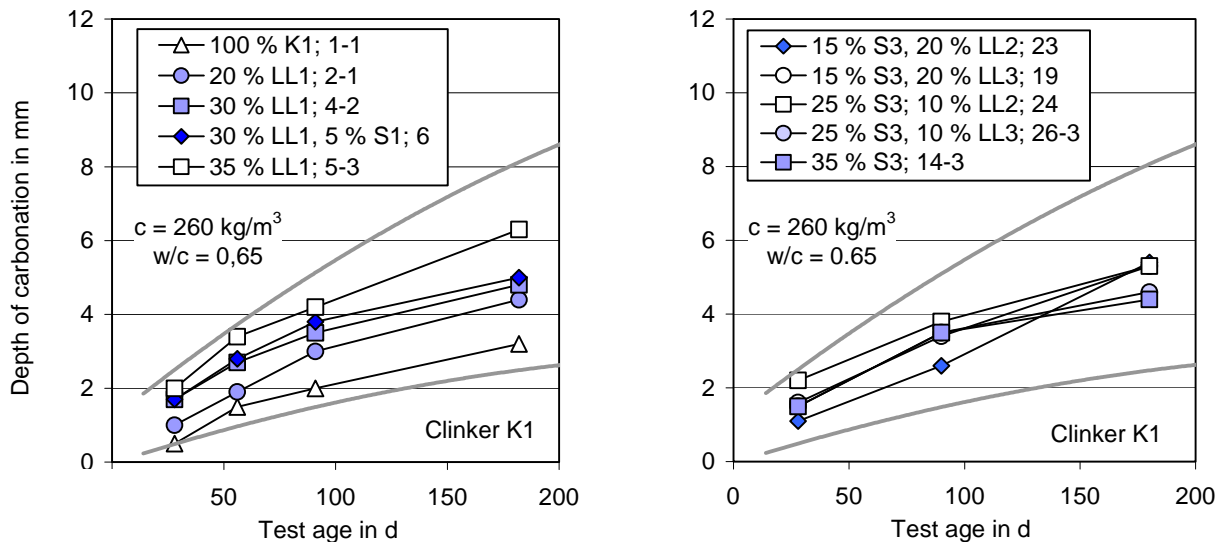


Figure 26: Influence of cements containing limestone (LL), fly ash (V), silica fume (D) and ground granulated blastfurnce slag (S) on the total porosity and the pore size distribution of cement paste compared to cement paste with Portland cement. Data: [Mül05, Sch98] Compiled by VDZ

Even the increased fineness of the clinker in filler-containing cement may positively influence the pore size distribution, compared to site blends of CEM I and filler.

2.2.4 Carbonation

Carbonation of concrete is a process by which carbon dioxide in the ambient air penetrates into the concrete and reacts with the hydroxides, such as calcium hydroxide, to form carbonates. In the reaction with calcium hydroxide, calcium carbonate is formed. Due to this reaction the pH-Value of the pore solution, which is higher than 12.5 due to the dissolved $\text{Ca}(\text{OH})_2$ and the alkalis, can decrease to values below 9 and therefore cause the depassivation of the reinforcement. In the presence of humidity and oxygen, corrosion can occur due to the depassivation caused by the low pH-value. The quality of the concrete cover is the decisive for the avoidance of corrosion. The quality of the concrete cover is composed by its thickness and the penetration resistance to CO_2 , which is mainly affected by the water cement ratio, but can also be influenced by the cement type or the use of additions respectively. The curing is of special importance. Even if there are differences in the carbonation depth of concrete using different cements (example: **Figure 27**), the depth of carbonation in good-quality, well-cured concrete for outside structures is generally of little practical importance, because CO_2 -diffusion and therewith carbonation depth decreases significantly with increasing moisture content (**Figure 29**).



Storage: 1 day in the mould, 6 days under water, climatic chamber at 20 °C / 65 % r.h. from 7th day
 } value range for concretes containing CEM I, CEM II/A-LL, CEM II/B-S, CEM III/A and CEM III/B acc. to [Sta95, Man98]

Figure 27: Development with time of the depth of carbonation in concretes made using Portland cement and Portland-limestone cements (left) and various Portland-composite cements (right) [Mül05]

Fly ash or blended cement containing fly ash may exhibit higher carbonation rate at early ages (**Figure 28**). However, with increasing reaction with time of the fly ash component, the densening effect becomes more pronounced, reducing the carbonation rate. Norwegian results [Maa87] stated that blended cement with up to 20-25 % fly ash even at younger ages were not more susceptible to significantly increased carbonation, due to the higher fineness of such cement – in contrast to blends of fly ash and CEM I cements at concrete ready mix stations.

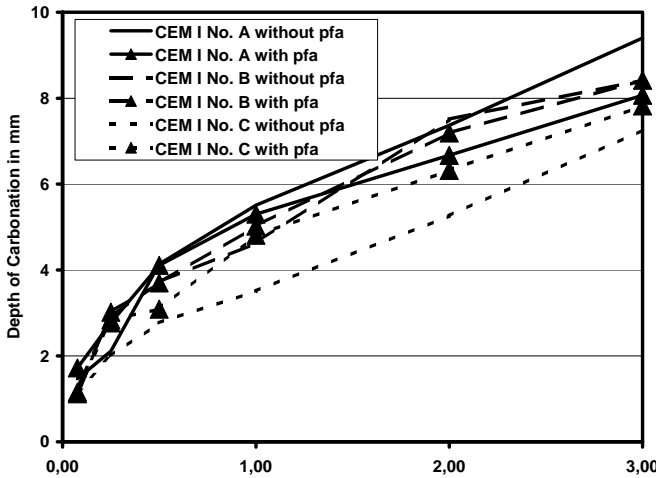


Figure 28: Influence of fly ash with CEM I on depth of carbonation ($w/c = 0,60$, $w/(c+0,5 \times pfa) = 0,60$, $c = 300 \text{ kg/m}^3$, $[c+pfa] = 240 + 60 \text{ kg/m}^3$) [Här95]

Inside buildings, carbonation depth can - and may be allowed to be - be much higher than for concrete surfaces exposed to water. In these cases the corrosion risk is low even with higher carbonation depth, because of the low humidity (**Figure 30**).

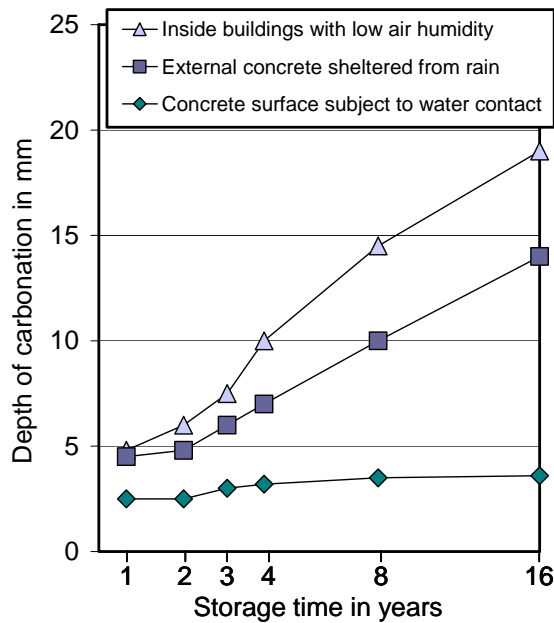


Figure 29: Influence of exposure on carbonation depth [Bak91]

Depth of carbonation and risk of corrosion

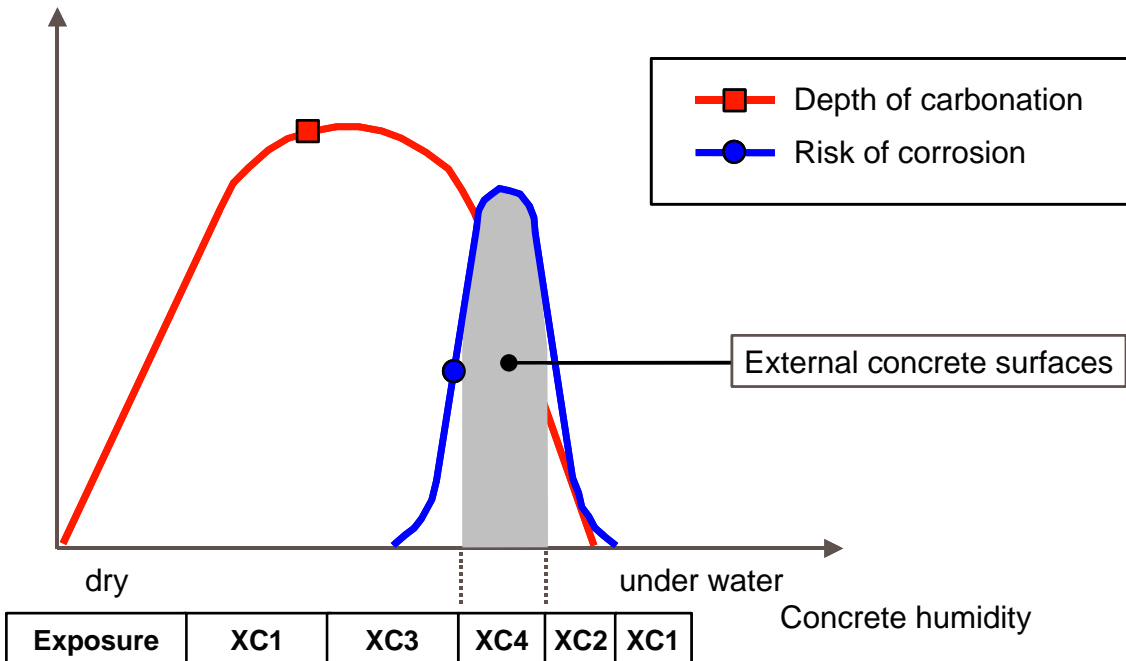


Figure 30: Influence of exposure on carbonation depth
 [Compiled by Christoph Müller, VDZ]

2.2.5 Penetration of chlorides

Chlorides can reach into the concrete from the use of de-icing salts, from seawater or from the air (e. g. sea-air, PVC-Fire). In the presence of humidity and oxygen, corrosion can occur due to a critical free chloride content at the surface of the reinforcement. As in the case of carbonation, the quality of the concrete cover is decisive for the avoidance of corrosion.

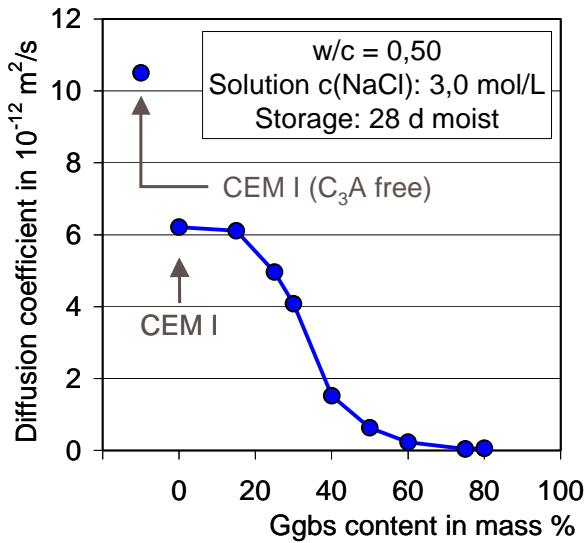


Figure 31: Influence of ggbs on the diffusion coefficient for chloride [Bro83]

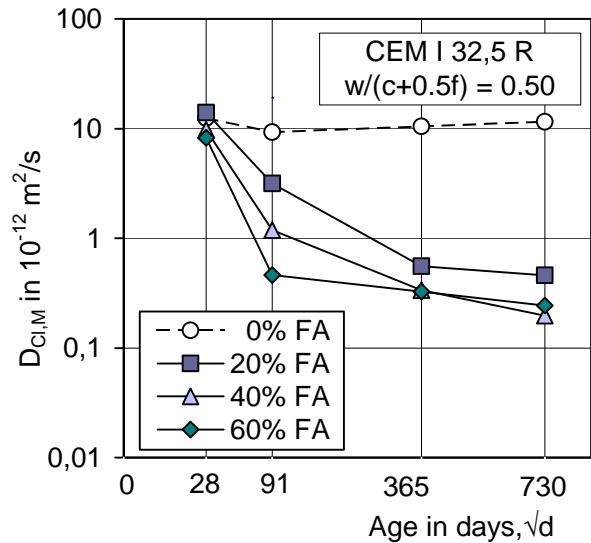


Figure 32: Influence of fly ash (FA) on the migration coefficient for chloride [Wie00]

The use of cements containing ggbs or fly ash can result in a significant increase in the resistance against chloride penetration (**Figures 31 and 32**). This can be attributed to the reduction of capillary pores and the higher amount of finer pores in the cement paste when using these cements (**Figure 26**). Besides the higher density of mortar and concrete with cements containing ggbs or pfa these cements are able to bind more chloride chemically within the C-S-H phases than Portland cement [Gun92]. **Figures 32 and 33** show 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 $18 \times 10^{12} \text{ m}^2/\text{s}$. 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 [Mül06].

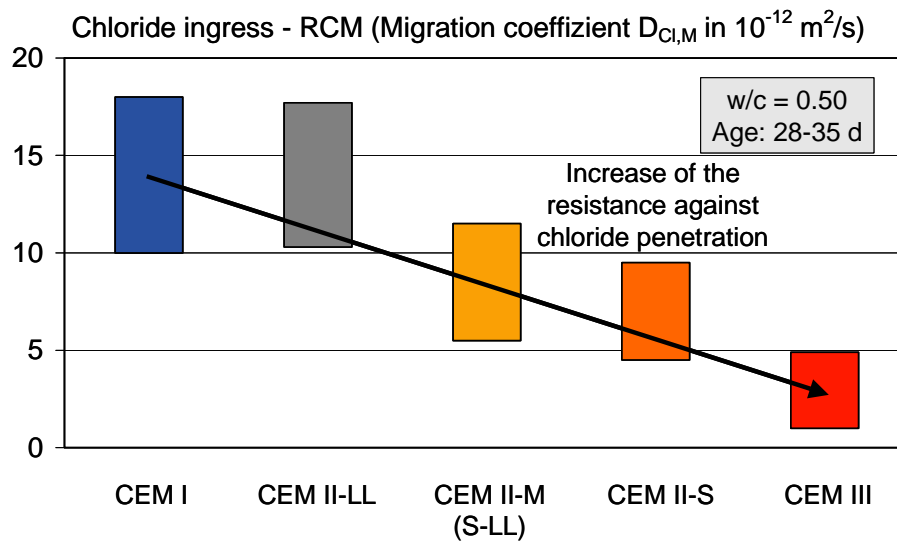


Figure 33: Chloride migration coefficient $D_{Cl,M}$ of concretes with $w/c = 0.50$ and $c = 320 \text{ kg/m}^3$ – water storage [Mül06]

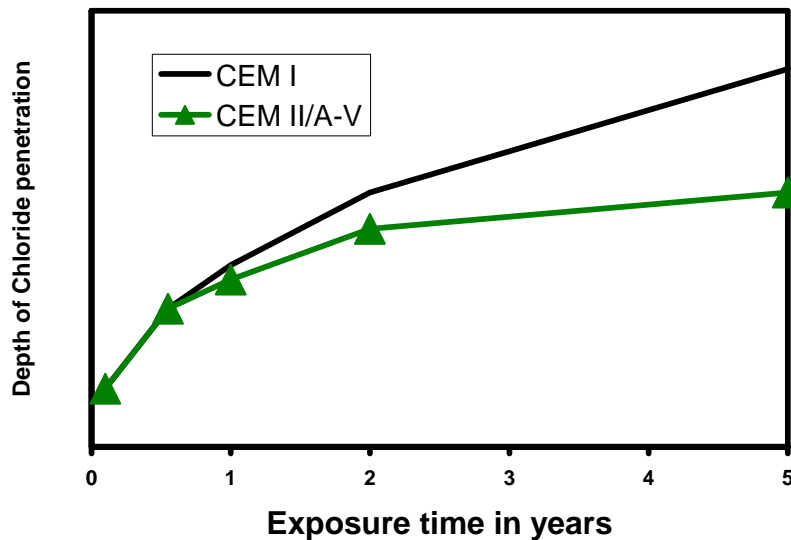


Figure 34: Concrete for marine environment ($w/c = 0,45$) with CEM I and CEM II/A-V (20 % pfa) stored under natural conditions in marine tidal water zone outside Trondheim, Norway [Source: NORCEM AS]

The depth of penetration of 0,1% Cl^- -ions shows, that blended cement CEM II/A-V (20 % pfa) exhibits nearly full stop in chloride penetration after some years (**Figure 34**).

The effect of Portland-pozzolanic cement is, similarly to Portland-fly ash cement (**Figure 34**), positive according to concrete’s chloride permeability (**Figure 35**). It seems that natural pozzolana is able to bind chlorides even when it is used in lower quantities (in the case of concrete manufactured with CEM II/B-M 32,5 (P-W-LL)).

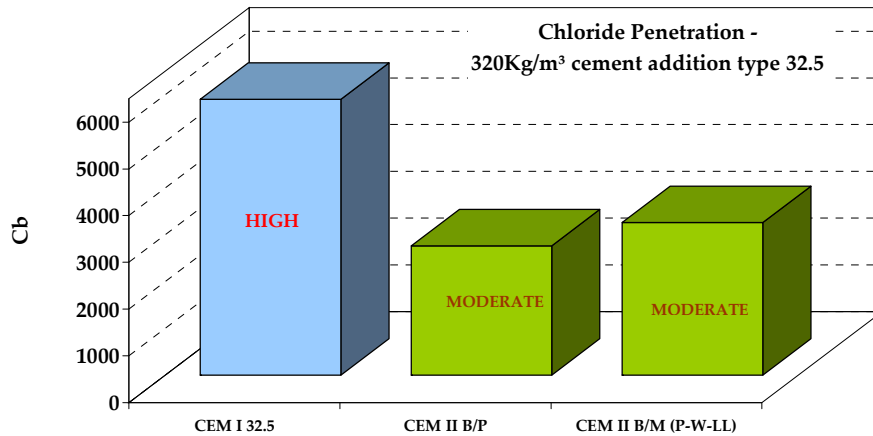


Figure 35: Chloride permeability according to ASTM C 1202-97 “Rapid Chloride permeability test” – Source: Titan Cement

2.2.6 Resistance to freezing and thawing

2.2.6.1 General

Concrete used in structures and pavements is expected to have a long life and low maintenance. It must have good durability to resist anticipated exposure conditions. One of the most potentially destructive weathering factor in some European countries is freezing and thawing while the concrete contains a certain amount of water, particularly in the presence of deicing chemicals. Deterioration is caused by the freezing of water and subsequent expansion in the paste, the aggregate particles or both.

2.2.6.2 Freeze thaw resistance

The main factor influencing the freeze/thaw resistance of concrete is its porosity which is mainly affected by the water to cement ratio (**Figure 36**).

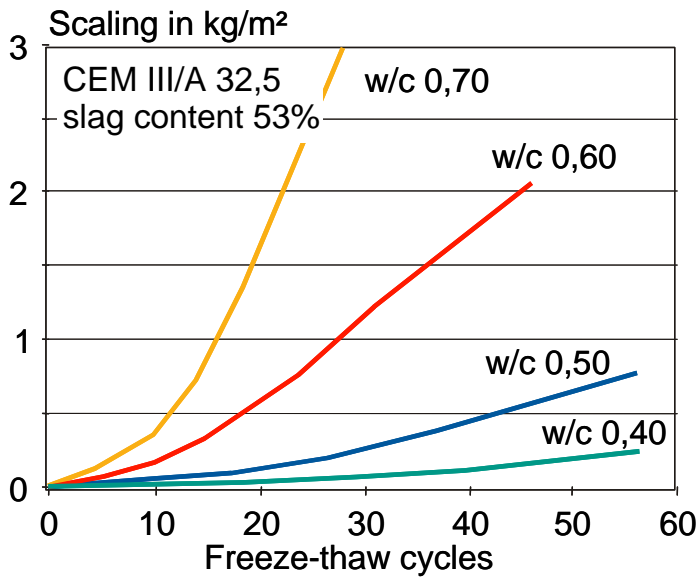


Figure 36: Scaling of concrete measured with CF test according to prEN 12390-9 dependent on the water to cement ratio [Aub99]

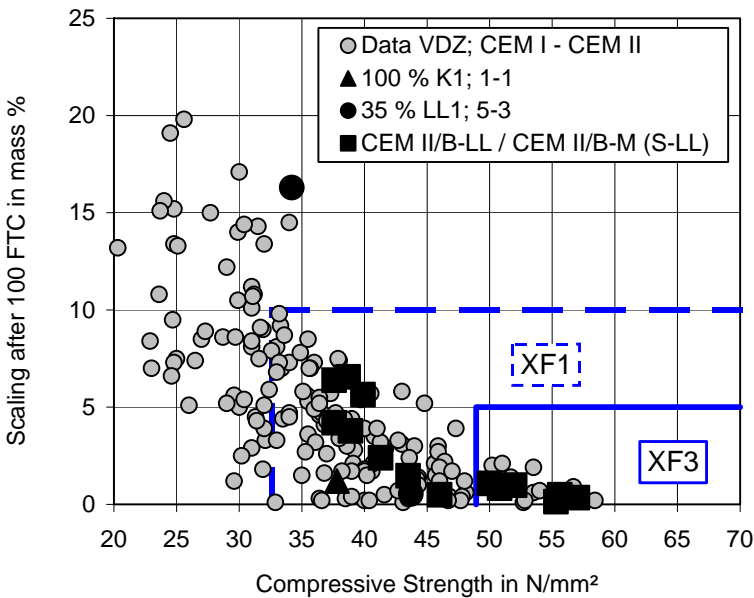


Figure 37: Relationship between scaling (cube test) and the concrete compressive strength at 28 d [Mül05]

There is – to some extent – a correlation between the water cement ratio and the concrete compressive strength and therefore also between the concrete compressive strength and the scaling mainly independent on the cement composition (**Figure 37**). Within the limiting values for the composition and the concrete properties of EN 206-1 and the NADs of many European countries, a lot of the blended cements used in Europe can be used for concrete with a high resistance against freezing and thawing.

The left-hand side of **Figure 38** 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 substantiated. 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) [BAW04] 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 %.

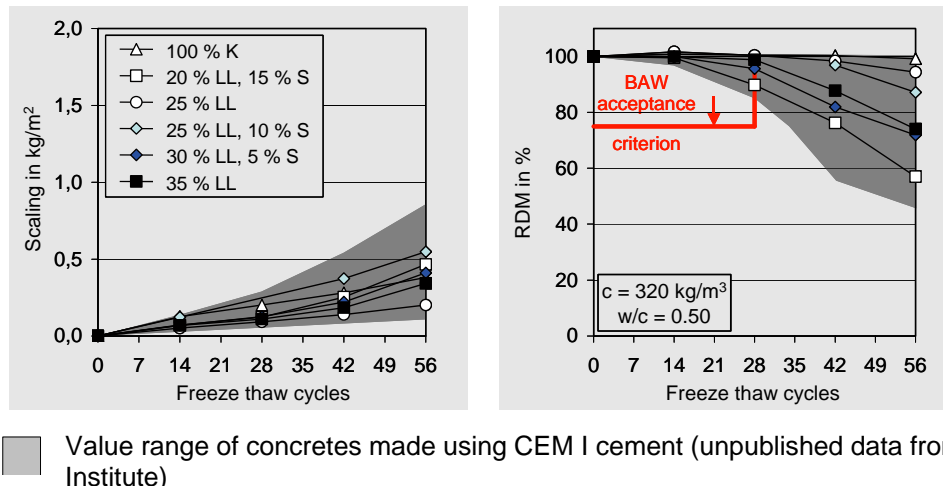


Figure 38: Scaling loss (left) and relative dynamic elastic modulus RDM (right) of concretes made using Portland cement and Portlandlimestone cements as well as various Portland-composite cements – CIF test [Mül06]

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 (**Figure 38, right**).

In Italy in the period 1941 – 2001 have been realised 72 dams, of which almost 50 with pozzolana based cements. No problems of freeze/thaw resistance have been reported for any of that dams.

2.2.7 Freeze/thaw resistance with de-icing salts

The main factor influencing the freeze/thaw resistance of concrete in presence of de-icing salts is the existence of an adequate artificial air void system (**Figure 39**).

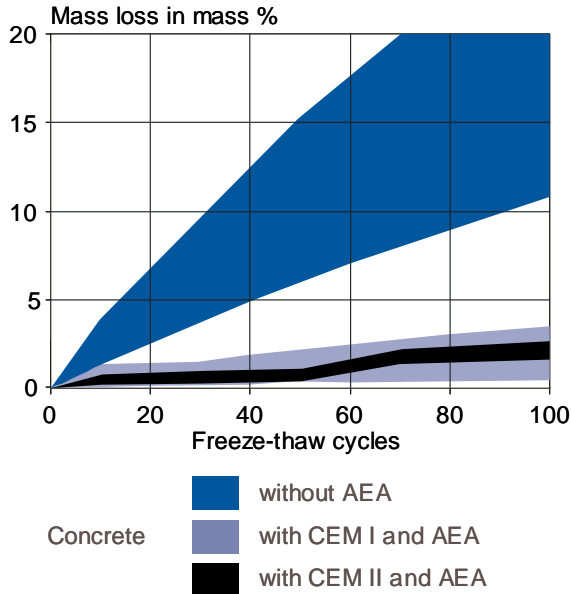


Figure 39: Scaling of concrete measured with cube test in 3% NaCl according to prEN 12390-9 [VDZ]

The freeze/thaw resistance with de-icing salts of concrete with blastfurnace cements with higher contents of gbs is reported to be lower than the resistance of concrete with CEM I or other blended cements (**Figure 40**). For that reason, e. g. the German NAD to EN 206-1 limits the use of blastfurnace cements for the exposure class XF4 to strength class $\geq 42,5$ or strength class 32,5 R with a content of granulated blastfurnace slag ≤ 50 % (m/m). Decisive for a low scaling of concrete exposed to freezing and thawing with de-icing salts is a high quality of the surface mortar. Of overall importance is a low water cement ratio, an adequate artificial air void system and an intensive curing, which is sufficiently long.

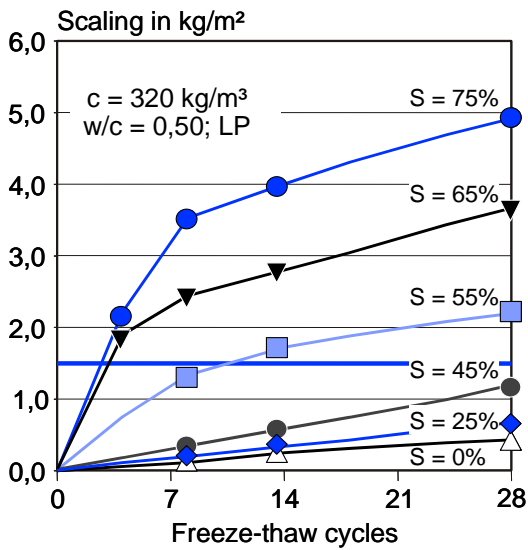


Figure 40: Scaling of concrete measured with CDF test according to prEN 12390-9 [Lud96]

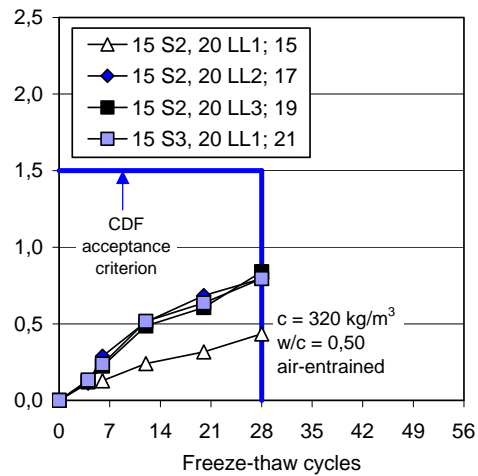
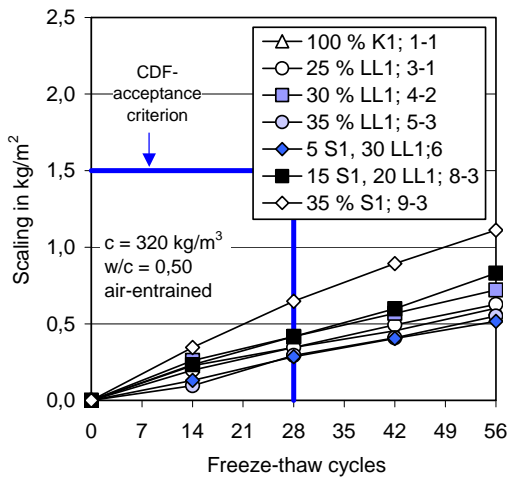


Figure 41: Scaling of concretes made using Portland cement and Portland-limestone cements (left) or various Portland-composite cements (right) CDF-Test [Mül05]

Figure 41 illustrates, that concrete with Portland limestone cements or Portland composite cements with up to 35 % gbs and limestone shows a scaling in the range of concrete with Portland cement.

3 Blended cements or blending cements ?

The use of blended cements offers numerous benefits for the cement producer, the ready-mix-concrete producer and the end-user. The overall environmental benefit results from the reduction of the specific CO₂-emissions of cement and concrete. This ecological aspect is not the only argument in favour of blended cements. They are also viable alternatives to Portland cement from the technical point of view. The influence exerted by different main constituents of cement on concrete properties has been 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 single cement type – 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 blended cements particularly well suited for different applications in concrete. This process requires an integrated assessment of all requirements to be met by cements during manufacture and application. From a technical perspective this includes the strength formation potential as well as good workability of the concrete and, in particular, the durability of the concrete made from these cements. The set of different properties available with these materials advocates the marketing of a palette of products to provide adequate work design for different applications.

The user of blended cements gets one optimized and quality controlled product from one source. Cement producers possess knowledge on the production of blended cements over decades. The use of slag cements in Germany can be taken as an example. By means of the collaboration of the cement producer and the producer of the granulated slag as well as the quality control of the granulated slag by the cement producer variations in the quality of the granulated slag with regard to the chemical and mineralogical composition are detected and balanced by adequate measures during cement production.

The following provisions can be used by the cement producer:

- Variation of the fineness of clinker and granulated slag by means of joint grinding or separate grinding and subsequent blending;
- Variation of the composition (increase or decrease of the slag content);
- Variation of the amount and the composition of the calcium sulfate.

Main constituents in cement are thus adjusted with regard to particle size distribution and sulphate content. Therefore e. g. setting time is controlled when using blended cements instead of blending cements – which means e. g. the use of Portland cement and ground granulated blastfurnace slag as a concrete addition.

If generally and which control factors would be usable in concrete production in practice using ground granulated blastfurnace slag as a concrete addition in Germany and if this would lead to the same flexibility and reliability compared to the use of slag cements is completely unknown due to a lack of practice.

4 Environmental aspects

The advantages of blended cements with regard to CO₂ emissions have been discussed in chapter 1.1. A question often raised is, whether the use of other main constituents besides clinker influence the behavior of concrete in contact with soil, ground water or drinking water. With regard to these aspects, the leaching behaviour of concrete has to be discussed.

The question as to whether heavy metals contained in concrete could leach out has long been a subject of scientific investigation. Many tests and studies carried out by independent scientists have been reported in Europe and North America. Even when concrete was artificially spiked with heavy metals (up to 1000 times the average concentrations), leaching has always been found to be either immeasurable or significantly below levels allowed for drinking water – the most stringent regulation. Concrete has thus been proved, by independent bodies, to comply with the most stringent levels of health requirements [CEM06].

The topic of environmental impact from cement-based materials to soil and groundwater forms an aspect to be addressed *also* under Essential requirement number 3 of the Construction Products Directive (CPD), which focuses on Health & Environment aspects. This aspect has been covered in Cluster 1 *of the ECOServe network* in relation

to deriving criteria for acceptance of waste as alternative fuel or alternative raw material for cement production. Total content of *substances in* cement is not a suitable property to assess environmental impact, as large differences in release of substances may exist between cement mortars produced with the same chemical composition. The test methods to be used to address environmental impact to soil and groundwater are leaching tests on the final product. So testing by leaching is not done on cement, but on a cement mortar sample (EN 197).

In evaluating test methods for a wider range of utilisation and disposal scenarios in another context (Harmonisation project, ECRICEM II, GRACOS, SAMARIS, LeachXS, HORIZONTAL - [Dij05, Kos02, Slo97, Slo04, Slo05]), it was found that a limited set of characterisation leaching tests would provide the necessary information to address these questions. A major distinction in testing is related to the nature of the material - being granular or monolithic. This requires a different testing approach, as for granular material percolation is generally the dominant release mechanism, while for monolithic materials the surface processes and diffusion are more important. For an understanding of changes in release resulting from external influences (e. g. carbonation, oxidation) a pH dependence leaching tests has been developed. The combination of these tests allows many questions related to utilisation of products in different settings to be answered.

In parallel to the work on regular Portland cement mortars collected in Cluster 1, also information on blended cements has been obtained. The testing to be carried out is not different for blended cement mortar or CEM I mortar specimen. In **Figure 43** a comparison of regular CEM I and blended cements is given showing good consistency between the data. The main difference is the leaching of Cr VI, which due to the reducing properties of slag in case of cements blended with blast furnace slag is far less than from CEM I cements and even less than Cr treated cements by application of additives. This is good for the long term behaviour of construction debris as Cr leaching will remain low owing to the conversion from Cr III to Cr VI progressing swiftly at high temperature, but is rather slow or not at all at room temperature. In **Figure 42** the pH and ANC data for the same cement mortars is given, which shows that the ANC of the slag blended cements is lower than that of regular Portland cement.

Results shown in **Figure 43** and **Figure 42** can be summarized as follows:

- Leaching of major, minor and trace elements from all cement-based materials - CEM I, CEM II, CEM II, CEM IV - is quite systematic. The testing approach, modelling and scenario evaluation is equally applicable for regular Portland cement mortar and for blended cement mortars.
- Blended cements based on Blast Furnace slag feature low Cr VI leachability resulting from the inherent reducing properties of blast furnace slag that will transform any Cr VI produced in the cement kiln to Cr III.
- The Acid Neutralisation Capacity (ANC) of cement mortar blended with blast furnace slag is generally lower than that of regular Portland cement.

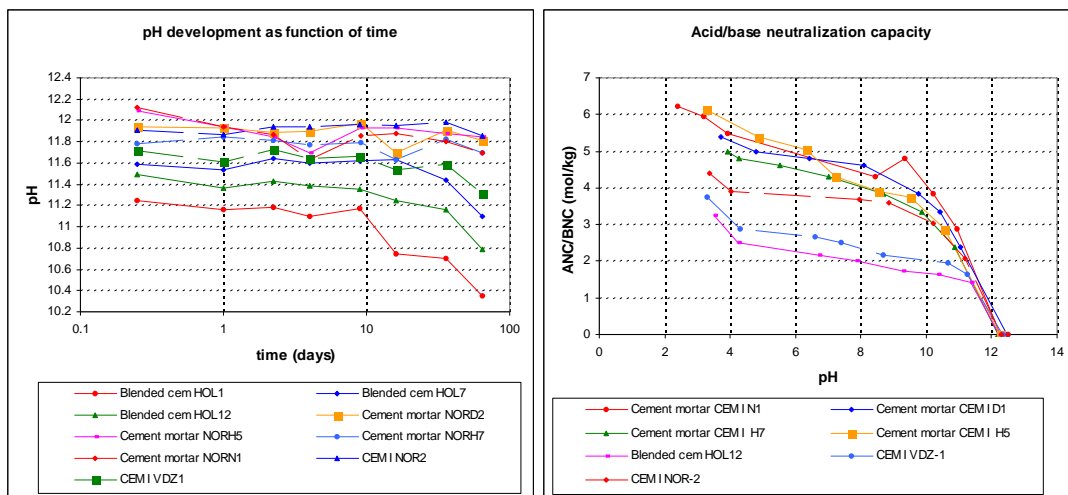


Figure 42: pH and ANC measurements in CEM I and blended cements.

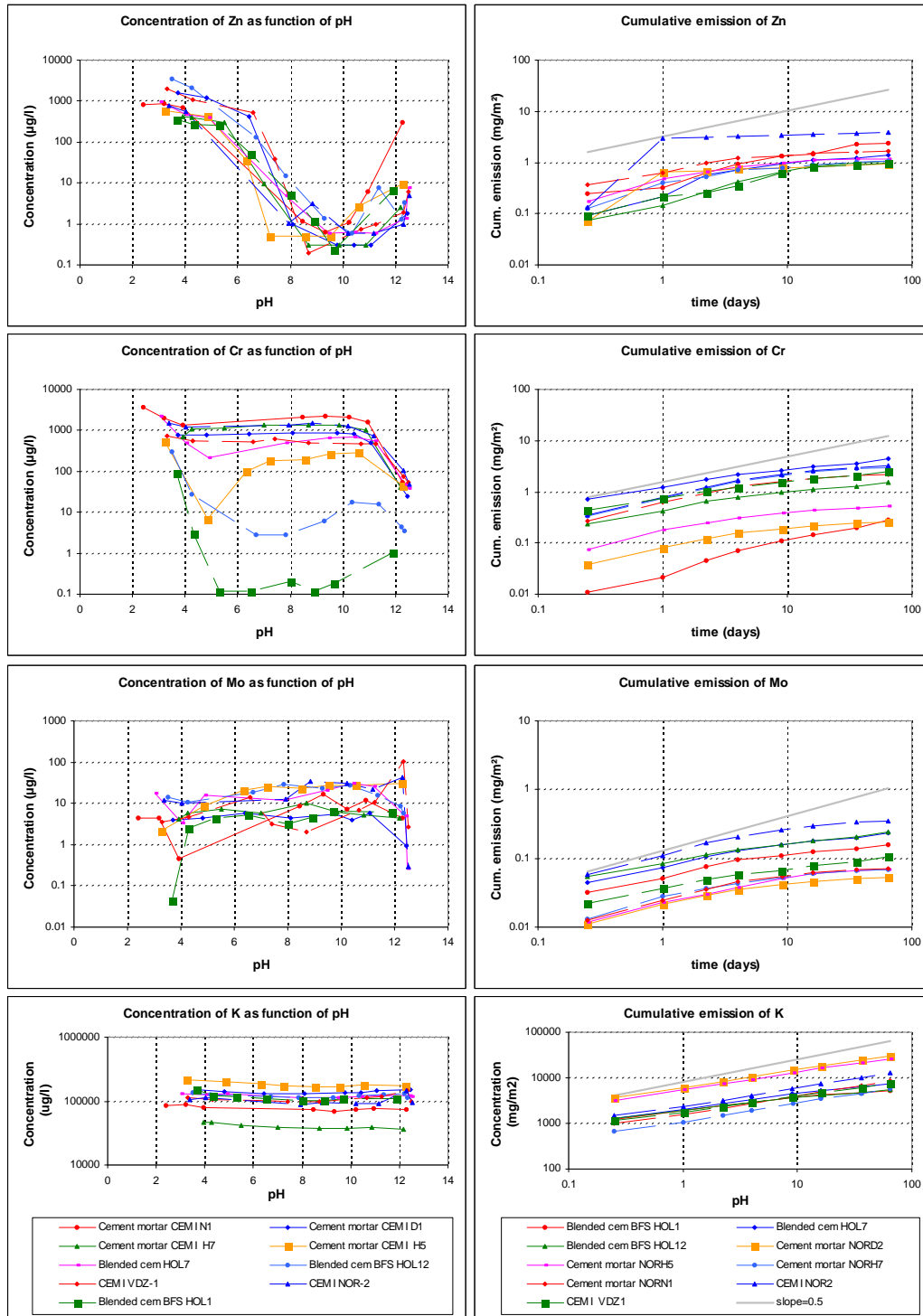


Figure 43: Comparison of leachability of CEM I and a selection of blended cements as a function of pH and as a function of L/S.

5 Application of blended cements

In order to document the performance of blended cements, examples for applications of blended cements in outstanding engineering work were compiled (**Table 1**) In most countries, which provided examples blended cements are so much diffused that a list cannot be representative of the outstanding engineering work; in any case some examples are given.

Table 1: Examples for the application of blended cements in construction engineering

Country	City / Region	Building / Construction	Component	Year of construction	Cement type	Concrete batch/ Length
1	2	3	4	5		
DE	near Hagen Westhofener Kreuz	Lennetalbridge, Federal motorway A 45	Superstructure	1965-66	EPZ 375 (today CEM II/A-S)	ca. 1,0 km length ca. 25.000 m ³
DE	near Wilhelmshaven	Federal motorway A 29	Concrete pavement	1979	EPZ 35 F (today CEM II/B-S)	ca. 18.000 m ³
DE	near Bitburg	Kylltalbridge, Federal motorway A 60	Arch and columns	1995-99	CEM II/B-S 42,5	ca. 30.000 m ³
DE			Bridge caps		CEM II/B-S 32,5 R	ca. 150 m ³
DE	Stuttgart	Landesgirokasse, Kronprinzenbau (Fair- faced concrete)	Walls, Columns	1994	CEM II/A-LL 32,5 R	ca. 200 m ³
DE	Überlingen	Prestressed concrete bridge B 31	Superstructure	1998	CEM II/A-LL 32,5 R	ca. 1045 m ³
DE	Stuttgart	Federal road B 312	Bridges with caps	1990-95	CEM II/B-T 32,5 R und CEM II/B-T 42,5 (both Terrament®)	ca. 70.000 m ³
DE	Jettenbach / Töging	Inn channel restoration	Channel side faces, Partly floor level	2003	CEM II/B-S 32,5 R	150.000 m ³
DE	Leibis Lichte	Dam	Concrete dam	2002-2006	CEM II/B-S 32,5 R-NA	630.000 m ³
DE	Eastern Germany	Bridge for the federal road B6n	Counter Bearing Bridge deck	2005	CEM II/B-M(S-LL) 32,5 R-AZ	ca. 520 m ³
DE	Quedlinburg	Bridge for the federal road B6n	Counter Bearing (fair-faced concrete)	2005	CEM II/B-M(S-LL) 32,5 R-AZ	ca. 300 m ³

ECOserve - Cluster 2 “Blended cements”

DE	Uelzen	Sluice	Core concrete Cladding components	2001-2005	CEM III/A 32,5 N-LH/NA CEM II/B-S 32,5 R	200.000m ³
GR	Rio Antirio	Rio-Antirio Bridge	Whole structure but the deck slab	1998-2004	CEM III/A-42.5 N	ca. 210.000m ³
GR	Thessaloniki	Egnatia Highway bridges	Whole structure	2001-05	CEM II/A-42.5 N	ca. 500.000m ³
I	Piemonte North of Italy	Motorway Asti – Cuneo (Links to A6 and A21)	All	Work in progress	CEM II/A-LL 32.5 R CEM II/A-LL 42.5 R	ca. 150.000 m ³
I	Pescara Centre of Italy	Church (Self Compacting Concrete)	All	2001	CEM II/A-LL 42.5 R White cement	ca. 20.000 m ³
I	Campania – Calabria South of Italy	Motorway A3	Emergency lane	Work in progress	CEM II/A-LL 32.5 R CEM II/A-LL 42.5 R	ca. 600.000 m ³
No	Finnmark	Statoil "Snow White" Storage tanks for natural gas storage terminal, Air entrained concrete		2001	CEM II/A-V 42,5 R	n. i. a.
No	Westcost	Triangle bridge / island connecting structure		2004	CEM II/A-V 42,5 R	n. i. a.
PI	Patnow II	Coal-based electric power station	foundation of boiler	2002	CEM III/A 32.5 NA	size 46x46x3.5m
PI	Wroclaw	Millenium bidge over Odra River	foundation	2002-2004	CEM III/A 32.5 NA	1400m ³
PI	Wroclaw	Millenium bidge over Odra River	pylons and deck of suspended bridge	2002-2004	CEM II-B/S 42.5 N	pylons 50m high the longest span 153m
PI	Bedzin	LAGISZA electric power plant	foundation of supercritical FBC boiler	2006	CEM III/A 32.5 NA	7000m ³

n.i.a.: no information available

6 References

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Table A1: The 27 products in the family of common cements acc. to EN 197-1

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass ^a)											Minor additional constituents
			Main constituents											
			Clinker K	Blast-furnace slag S	Silica fume D ^b	Pozzolana		Fly ash		Burnt shale T	Limestone			
natural P	natural calcined Q	siliceous V				calcareous W	L	LL						
CEM I	Portland cement	CEM I	95-100	-	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM II/A-S	80-94	6-20	-	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	-	0-5
		CEM II/B-P	65-79	-	-	21-35	-	-	-	-	-	-	-	0-5
		CEM II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-V	65-79	-	-	-	-	21-35	-	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	-	0-5
	Portland-burnt shale cement	CEM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-T	65-79	-	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-limestone cement	CEM II/A-L	80-94	-	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-LL	65-79	-	-	-	-	-	-	-	-	-	21-35	0-5
	Portland-composite cement ^c	CEM II/A-M	80-94	<----- 6-20 ----->										0-5
CEM II/B-M		65-79	<----- 21-35 ----->										0-5	
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement ^c	CEM IV/A	65-89	-	<----- 11-35 ----->						-	-	-	0-5
		CEM IV/B	45-64	-	<----- 36-55 ----->						-	-	-	0-5
CEM V	Composite cement ^c	CEM V/A	40-64	18-30	-	<----- 18-30 ----->			-	-	-	-	-	0-5
		CEM V/B	20-38	31-50	-	<----- 31-50 ----->			-	-	-	-	-	0-5

a The values in the table refer to the sum of the main and minor additional constituents.
b The proportion of silica fume is limited to 10 %.
c In Portland-composite cements CEM II/A-M and CEM II/B-M, in pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

Table A2: Areas of application of cements conforming to EN 197-1 in concrete conforming to EN 206-1 and varois national annex – Example: Exposed vertical surface of inland concrete with no significant levels of external chlorides [Mül06] ¹⁾

Country	Exposure class	min f _c	max (w/c) _{eq}	min c kg/m ³	CEM I	CEM II															CEM III			CEM IV		CEM V			
						S		D	P/Q		V		W		T		LL		L		M		A	B	C	A	B	A	B
						A	B	A	A	B	A	B	A	B	A	B	A	B	A	B	A	B							
Austria	XC1+XF1	--	0,55	300	x	x	x	x			x	x	(x) ₂₎					x	(x) ₂₎		(x) ₂₎	x	(x) ₂₎						
Belgium	EE3 (XC4+XF1)	C30/37	0,50	320	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x					
Czech Republic	XC1 to XC4 or XF1	C30/37	0,50 or 0,55	300	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x						
Denmark	(XC2, XC3, XC4, XF1, XA1)	C25/30	0,55	150 ³⁾	(x) ⁴⁾						(x) ₄₎	(x) ₄₎				(x) ₄₎		(x) ₄₎											
Finland	XC3 or XC4, XF1	C25/30	0,60	250 ⁵⁾	x	x	(x) ₆₎	x			x	(x) ₆₎				x ₆₎			x	(x) ₆₎									
Germany	XC4 + XF1	C25/30	0,60	280	x	x	x	x	x	x	x	x	○	○	x	x	x	○	○	○	(x) ₇₎	(x) ₇₎	x	x	○	○	(x) ₈₎	(x) ₉₎	(x) ₉₎
Ireland	XC2 or XC4 + XF1	C30/37 if XC4 + XF1	0,55	320	x																								
Italy	XC1	C25/30	0,60	300	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
	XC2 + XF1	C32/40	0,50	320	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	
Luxembourg	XC4 + XF1	C25/30	0,60	280	x	x	x	x		x					x		x			(x) ₁₀₎		x	x						
Netherlands	XC3	--	0,55	280	x	x	x				x	x			x	x						x	x						
	XC4 + XF1	--	0,50	300	x	x	x				x	x			x	x						x	x						
Norway	XC4 + XF1	--	0,60	250	x	x		x			x					x		x											
Portugal	XC4 + XF1 ¹¹⁾	C30/37	0,60	280	x	x		x	x		x		x		x		x		x										
			0,55	300	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₎		

