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**SUMMARY**

The aim of this research project was to produce and test, both in the laboratory and in the plant, cements containing levels of limestone beyond the maximum levels described in DIN EN 197-1. Limestone levels between 30 mass % and 70 mass %, relative to the cement including the sulfate agent, were used. The effect of reducing the clinker in the cement on the strength development and durability of the concrete was examined in relation to the properties of the limestone used as a further main constituent. The investigation focused on the extent to which the effect of replacing the clinker in the cement can be countered by optimizing the particle size and component distributions and adapting the concrete technology under laboratory and practical conditions. At the moment the situation can be summarized by stating that sophisticated process engineering measures in the cement plant and equally sophisticated concrete technology measures (low-water concrete with appropriate addition levels of admixtures) in the concrete production would be necessary for the production and use of high-limestone cements (up to 50 mass % LL). If these measures can be implemented under practical conditions then it will be possible for the concrete to achieve durability parameters that can meet the approval requirements. The robustness of these systems in construction work requires further verification. The creep and shrinkage of such concretes must be investigated in greater depth and the influence of the limestone quality on the results of freeze-thaw tests also requires further verification. The ecological balance values could be further improved by efficient utilization of the Portland cement clinker in cements containing high levels of limestone. In the balances drawn up for concretes with fairly low water/cement ratios using high-limestone cements the global warming potential for the same effectiveness (compressive strength and durability in the laboratory) is about 25 % lower than the global warming potential of a concrete made with CEM II/A-LL cement or with the average cement from the VDZ-EPD.

**ZUSAMMENFASSUNG**

Ziel des dargestellten Forschungsvorhabens war die labor- und werkseitige Herstellung und Prüfung von Zementen mit Kalksteingehalten jenseits der in DIN EN 197-1 beschriebenen Maximalgehalte. Es wurden Kalksteingehalte zwischen 30 M.-% und 70 M.-%, bezogen auf den sulfatträgerhaltigen Zement, verwendet. Die Auswirkung der Klinkerreduzierung im Zement in Abhängigkeit der Eigenschaften des Kalksteins als weiterem Hauptbestandteil auf die Festigkeitsentwicklung und die Dauerhaftigkeit von Beton wurde untersucht. Im Zentrum stand die Frage, inwieweit den Auswirkungen der Klinkersubstitution im Zement durch Optimierung der Korngrößen- und Komponentenverteilung sowie der Anpassung der Betontechnologie unter Laborbedingungen und unter praxisnahen Bedingungen begegnet werden kann. Zusammenfassend kann zum jetzigen Zeitpunkt festgestellt werden, dass für die Herstellung und Verwendung kalksteinreicher Zemente (bis 50 M.-% LL) anspruchsvolle verfahrenstechnische Maßnahmen im Zementwerk und ebenso anspruchsvolle betontechnologische Maßnahmen (wasserarmer Beton mit entsprechenden Zusatzmitteldosierungen) in der Betonherstellung erforderlich wären. Werden diese Maßnahmen unter Praxisbedingungen beherrscht, können zulassungsfähige Dauerhaftigkeitskennwerte am Beton erzielt werden. Die Robustheit derartiger Systeme im Baubetrieb bedarf einer weiteren Absicherung. Kriechen und Schwinden solcher Betone müssen weiter untersucht werden. Der Einfluss der Kalksteinqualität auf das Ergebnis von Frostversuchen bedarf ebenfalls einer weiteren Absicherung. Durch die effiziente Ausnutzung des Portlandzementklinkers in Zementen mit hohen Kalksteingehalten könnten die Werte einer Ökobilanz verbessert werden. In der Bilanzierung von Betonen mit niedrigeren Wasserzementwerten mit den kalksteinreichen Zementen liegt das Treibhauspotenzial bei gleicher Leistungsfähigkeit (Druckfestigkeit und Dauerhaftigkeit im Labor) rd. 25 % unter dem Treibhauspotenzial eines Betons mit CEM II/A-LL bzw. dem Durchschnittszement der VDZ-EPD.

(Translation by Robin B. C. Baker)

# Cements with a high limestone content – durability and practicability

## Zemente mit hohen Kalksteingehalten – Dauerhaftigkeit und praktische Umsetzbarkeit

## 1 Introduction

The cement industry throughout the world releases about 5 % of the carbon dioxide emissions caused by man. One way of limiting the discharge of $CO_2$ during the production of cement and concrete lies in the increasing production and use of cements containing several main constituents. The total emission of $CO_2$ per tonne of cement falls with efficient utilization of the Portland cement clinker in the cement. One problem is that two of the reactive main constituents, namely granulated blastfurnace slag and fly ash from bituminous coal, are only available in limited quantities and in Germany these materials are already practically fully utilized. It would therefore not be possible to make any further significant improvement in the environmental impact of a tonne of cement or a cubic metre of concrete in future by raising the proportion of CEM III or of CEM II-S and CEM II-V cements. Limestone, on the other hand, is available inexpensively and in nearly any quantity required. However, it is an inert material. This means that its proportion in cement cannot readily be increased significantly because of the conditions specified in the standards combined with the current lack of knowledge. It may also be necessary to differentiate between different grades of limestone.

The basic idea of the research project was to transfer the findings from the field of high-strength and ultra-high-strength concretes to normal structural concrete. The ratio of clinker to limestone in the cement was further reduced by modifying the current concrete technology constraints, in particular by reducing the water/cement ratio.

## 2 Trials and results

### 2.1 Cements and cement main constituents

CEM I 42,5 N, CEM I 52,5 R, CEM II/A-LL 32,5 R and CEM II/B-LL 32,5 R cements were used as reference cements. The test cements were produced by separate grinding and subsequent mixing of a CEM I 52,5 R cement and various grades of limestone (➧ Table 1). For the mortar trials the components were mixed in the laboratory but cements produced in the plant were used for the concrete trials. In the overview of the trials it became apparent that 50 mass % limestone in the cement represents a critical limit up to which it is still possible, by using appropriate sophisticated concrete technology, to produce durable concretes in the laboratory, so the results obtained with this limestone content are described below. The results obtained with 30 mass %, 35 mass %, 65 mass % and 70 mass % limestone are available in the final report on the research project.

### 2.2 Mortar properties

The compressive strengths of both standard mortars and of mortars made with cement contents and water/cement ratios deviating from the standard were tested after 2, 7 and 28 days as specified in DIN EN 196-1. Standard mortars with a water/cement ratio of w/c = 0.50 were produced

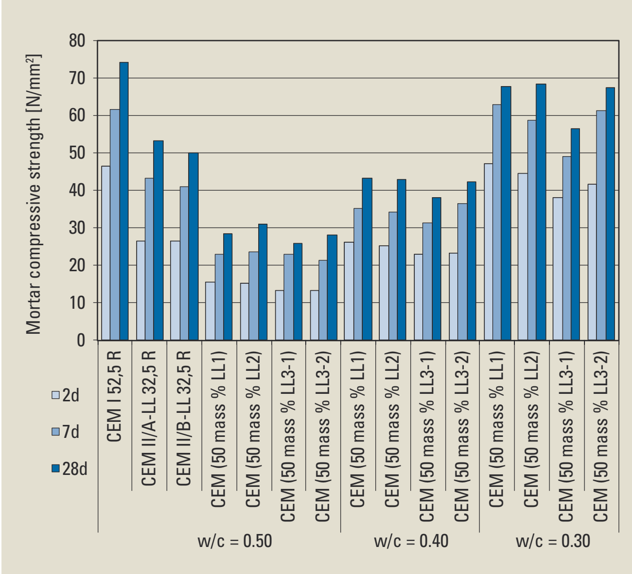


Figure 1: Strength development of mortars made with laboratory cements containing 50 mass % LL

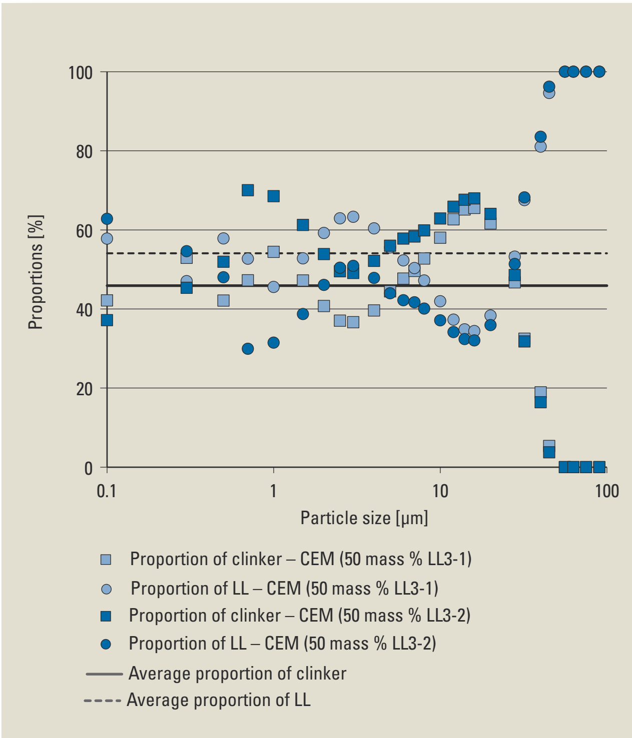


Figure 2: Combined particle size and component distributions

in accordance with DIN EN 196-1 with a cement content of 450 g per mix, in principle without the use of superplasticizers. Mortars with a water/cement ratio of w/c = 0.40 were produced with a cement content of 490 g per mix and mortars with w/c = 0.30 were produced with a cement content of 560 g per mix in order to maintain a constant paste content. A PCE-based superplasticizer was used to achieve a constant flow table spread of 130 ± 5 mm.

It can be seen from ❱ Fig. 1 that the laboratory cement made with LL3-2 limestone had compressive strengths similar to those of the cements made with LL1 and LL2 limestones and significantly higher strengths than the cements made with LL3-1. LL3-1 and LL3-2 are limestones of the same provenance but with different granulometries. This means that the strength development when using high levels of limestone beyond the maximum levels specified in DIN EN 197-1 is dependent less on the chemical composition of the limestone than on the particle size and component distributions of the main cement constituents.

Table 1: Characterization of the limestone from provenances 1 to 3

| | LL1 | LL2 | LL3-1 | LL3-2 | LL3-3 |
|---|---|---|---|---|---|
| $CaCO_3$ content in mass % | 98 | 88 | 75 | 75 | 75 |
| TOC in mass % | 0.02 | 0.05 | 0.1 | 0.1 | 0.1 |
| Methylene blue value in g/100 g | 0.03 | 0.50 | 0.60 | 0.40 | 0.40 |
| Blaine fineness in cm$^2$/g | 4200 | 4200 | 8000 | 5000 | 2700 |
| RRSB slope n | 0.8 | 0.9 | 0.7 | 0.7 | 0.6 |
| RRSB position parameter d´ in µm | 20 | 20 | 10 | 25 | 40 |

❱ Fig. 2 shows an example of component distribution in relation to particle size. The same clinker components were used for both cements. The proportions of the main cement constituents, namely clinker and limestone, in the cements containing 50 mass % of the LL3-1 or LL3-2 limestone are shown on the y-axis in relation to the particle size. The straight lines at 46 vol. % clinker and 54 vol. % limestone show the average volumetric proportions relative to the complete cement. Up to a particle size of about 30 µm the proportion of clinker in the cement containing LL3-2 is significantly higher than the 46 vol. % contained in the overall system while in this particle size range the clinker in the cement containing LL3-1 lies in about the same range as the above-mentioned average value. In particular, the cement containing LL3-2 has significantly higher proportions of clinker of up to about 70 vol. % in the size range to 10 µm that is crucial for the development of the early strength. The interlinking of the hydration products in the particle size ranges up to 10 µm and 30 µm is significantly less disrupted by inert particles when LL3-2 limestone is used. This means that a significantly higher strength can develop on all test dates under otherwise identical starting conditions. It is therefore of crucial importance that the particle size distributions of all the main constituents in the cement are carefully matched to one another.

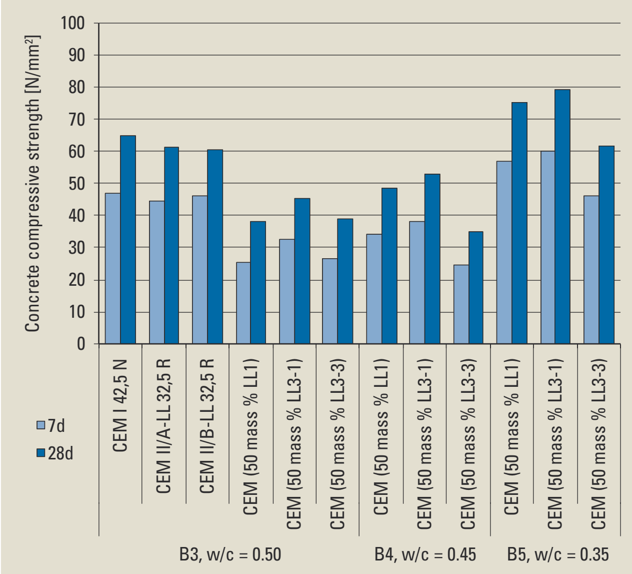


Figure 3: Compressive strength development of the concretes B3 to B5 under investigation

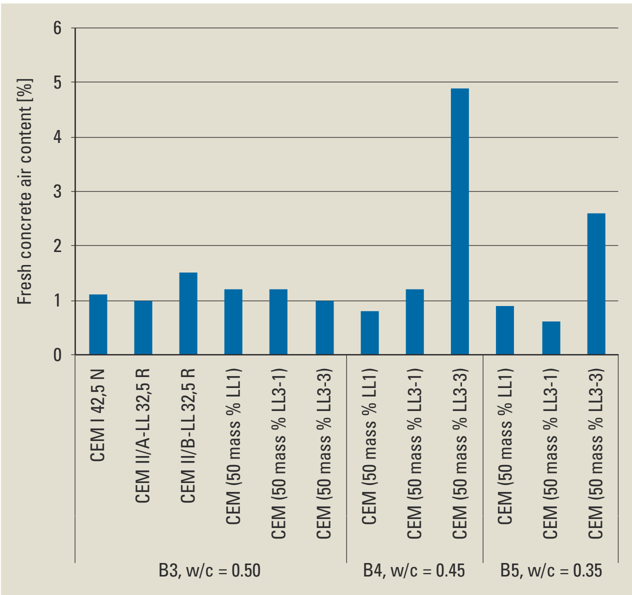


Figure 4: Fresh concrete air content of the concretes B3 to B5 under investigation

## 2.3 Concrete trials

Plant cements produced on an industrial scale were used for the concrete trials. The concretes were investigated on the same principle as the mortars. Firstly, the reference concretes were made up in accordance with the Tables F2.1 and F2.2 specified in DIN 1045-2. For the concretes made with the test cements the aggregate grading curve was optimized, the water/cement ratio was lowered while retaining the paste content and a constant flow table spread (consistency F4) was obtained by using a PCE-based superplasticizer. The concrete compositions are summarized in ❱ Table 2.

## 2.4 Concrete compressive strength

The concrete compressive strength was determined in accordance with DIN EN 12390-3 after 7 and 28 days on cubes with edge lengths of 150 mm. The results are shown in ❱ Fig. 3. Concretes made with CEM (50 mass % LL3-3) cement and water/cement ratios of w/c = 0.45 or 0.35 exhibited significantly lower strengths than the concretes made with CEM (50 mass % LL1) or CEM (50 mass % LL3-1) cements. The reason for this is the reproducibly higher air content of these concretes (cf. ❱ Fig. 4).This combination of superplasticizer and grade of limestone seems to have a tendency to form air voids. This type of behaviour is rare but has been observed occasionally in the laboratory. The reasons are not yet known.

## 2.5 Resistance to chloride penetration

The resistance to penetrating chlorides was determined by a rapid test method (migration test [1, 2]) on concretes B3 to B5. ❱ Fig. 5 shows that the chloride migration coefficients of concretes made with cements containing 50 mass % limestone can be the same as those of concretes made with the cements normally used in practice. For this the water/cement ratio has to be lowered to w/c = 0.35. The increased air content of the concrete made with CEM

(50 mass % LL3-3) cement (cf. Fig. 4) leads to significantly higher chloride migration coefficients that no longer lie in the same range as the reference concretes. This should be qualified by noting that the performance of the reference concretes with respect to their resistance to penetrating chlorides is not optimal for concretes that need a high chloride penetration resistance. Cements containing granulated blastfurnace slag perform better in this situation.

### 2.6 Freeze-thaw resistance

The freeze-thaw resistance of the concretes was measured by the CIF method as described by CEN/TR 15177. The scaling and relative dynamic modulus of elasticity were determined for up to 56 freeze-thaw cycles. The results are plotted in ❱ Figs. 6 and 7 as average values of five test specimens. In each case the results obtained with the reference concretes B3 made with CEM I 42,5 N, CEM II/A-LL 32,5 R and CEM II/B-LL 32,5 R cements are also shown for comparison.

Internal damage of the microstructure can normally be expected with freeze-thaw attack without the action of deicing agents if unsuitable starting materials or unsuitable concrete compositions are used [3]. This can be described by the relative dynamic modulus of elasticity. Fig. 6 shows that the freeze-thaw resistance of concretes made with cements containing 50 mass % limestone can be equal to that of concretes made with cements that are normally used in practice. For this the water/cement ratio has to be reduced to at least 0.45. Synthetic air voids can make a significant improvement to the freeze-thaw resistance. As described above, the superplasticizer used combined with the CEM (50 mass % LL3-3) cement led to the formation of air voids. The concretes made with CEM (50 mass % LL3-3) cement and superplasticizers (B4 and B5) do in fact show correspondingly low scaling and a slight drop in relative dynamic modulus of elasticity (Fig. 7) but are not directly comparable with the other concretes because of the air void content. The influence of the grade of limestone (which can be seen in Figs. 6 and 7 by comparing limestones LL1 and LL3) on the result of the freeze-thaw trials also requires further verification.

### 2.7 Carbonation

The carbonation tests were carried out on mortar prisms as described in DIN EN 196-1 (water storage until the seventh day). The depth of carbonation was measured after storage in a standard climate (20 °C and 65 % relative air humidity) at ages of up to 140 days. The water/cement ratios of cements containing high levels of limestone had to be reduced significantly to achieve the same depths of carbonation as the reference samples. Cements containing 50 and 60 mass %

Table 2: Concrete compositions

| | Concrete B3 | Concrete B4 | Concrete B5 |
|---|---|---|---|
| Cement content in kg/m$^3$ | 320 | 335 | 380 |
| Water/cement ratio | 0.50 | 0.45 | 0.35 |
| Paste content, incl. aggregate fraction <125 µm, in l/m$^3$ | 290 ± 5 | 290 ± 5 | 290 ± 5 |

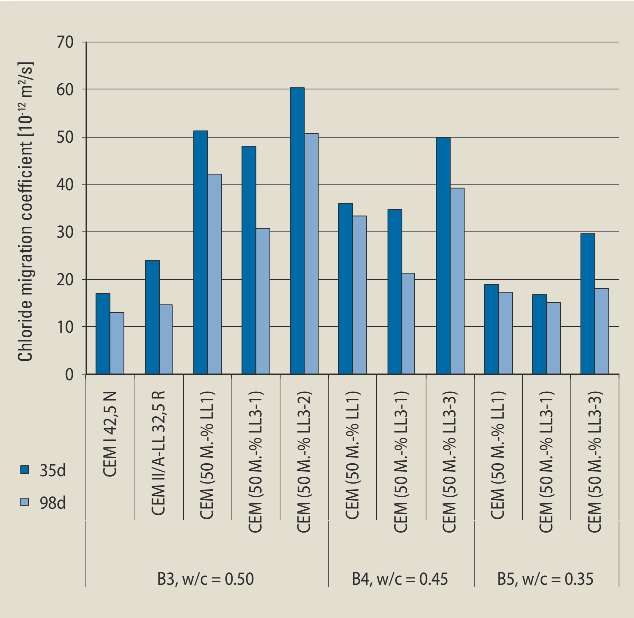


Figure 5: Chloride penetration resistance of concretes B3 to B5

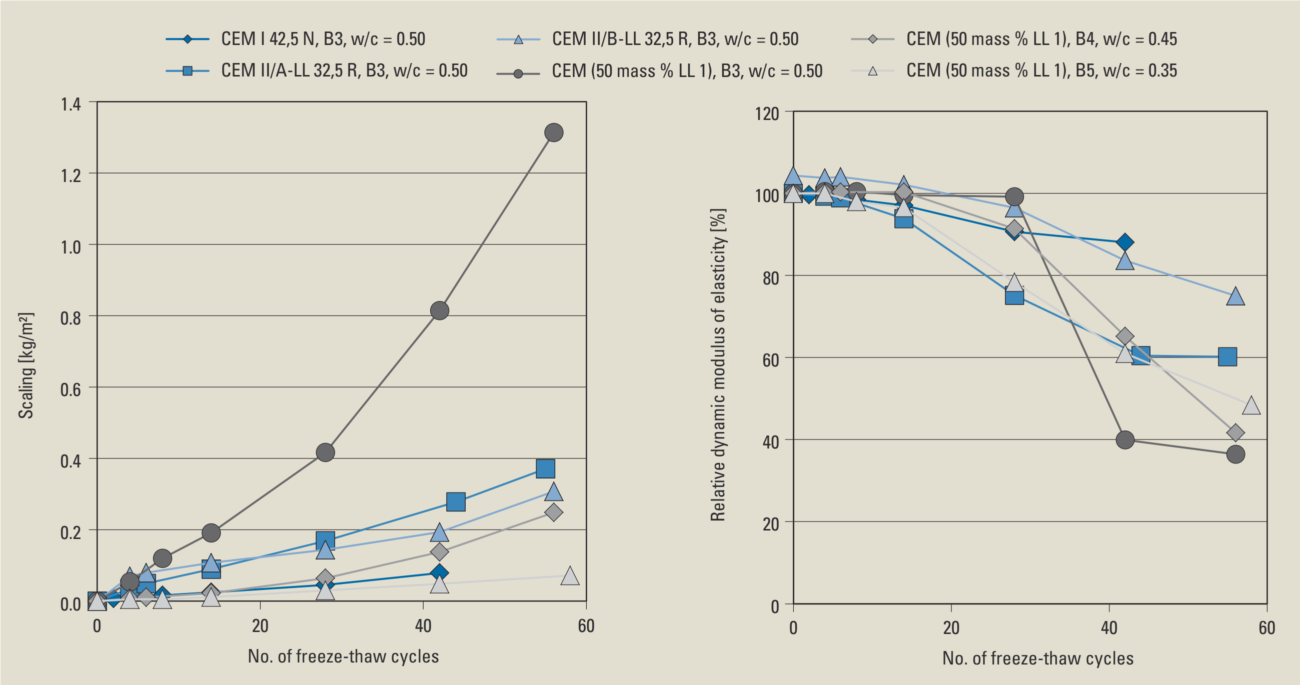


Figure 6: Scaling and relative dynamic modulus of elasticity of concretes B3, B4 and B5 made with cements containing 50 mass % LL1

limestone with water/cement ratios of w/c = 0.35 and w/c = 0.30 respectively achieved the same depths of carbonation as fine concretes made with CEM I, CEM II/A-LL and CEM II/B-LL cements with w/c = 0.50 (cf. equivalence lines in ❱ Fig. 8).

### 2.8 Creep and shrinkage

Two cylinders with dimension of diameter = 158 mm and length = 300 mm were used in each test to measure the shrinkage by the method described in DAfStb Vol. 422, section 2.6 and the creep by the method described in section 2.7. The specimens were left in the mould for one day after the manufacturing, then stored under water until the seventh day and subsequently stored at a temperature of 20 °C and a relative air humidity of 65 ± 2 %. The shrinkage was measured from the seventh day. A creep stress of $\sigma_u$ = ⅓ $f_{c,cyl}$ was applied at the age of 28 days for the creep trials.

The results of the investigation of the shrinkage and creep are summarized in ❱ Figs. 9 and 10. Concretes B4 and B5 made with CEM (50 mass % LL1) cement with water/cement ratios w/c = 0.45 and 0.35 respectively exhibit behaviour comparable to the reference concrete B3 made with CEM II/A-LL cement and a water/cement ratio w/c = 0.50 in terms of both shrinkage and creep. However, the concretes made with cements containing limestone of provenance 3 exhibited both greater shrinkage and greater creep on all test dates. In addition to the durability it is there-

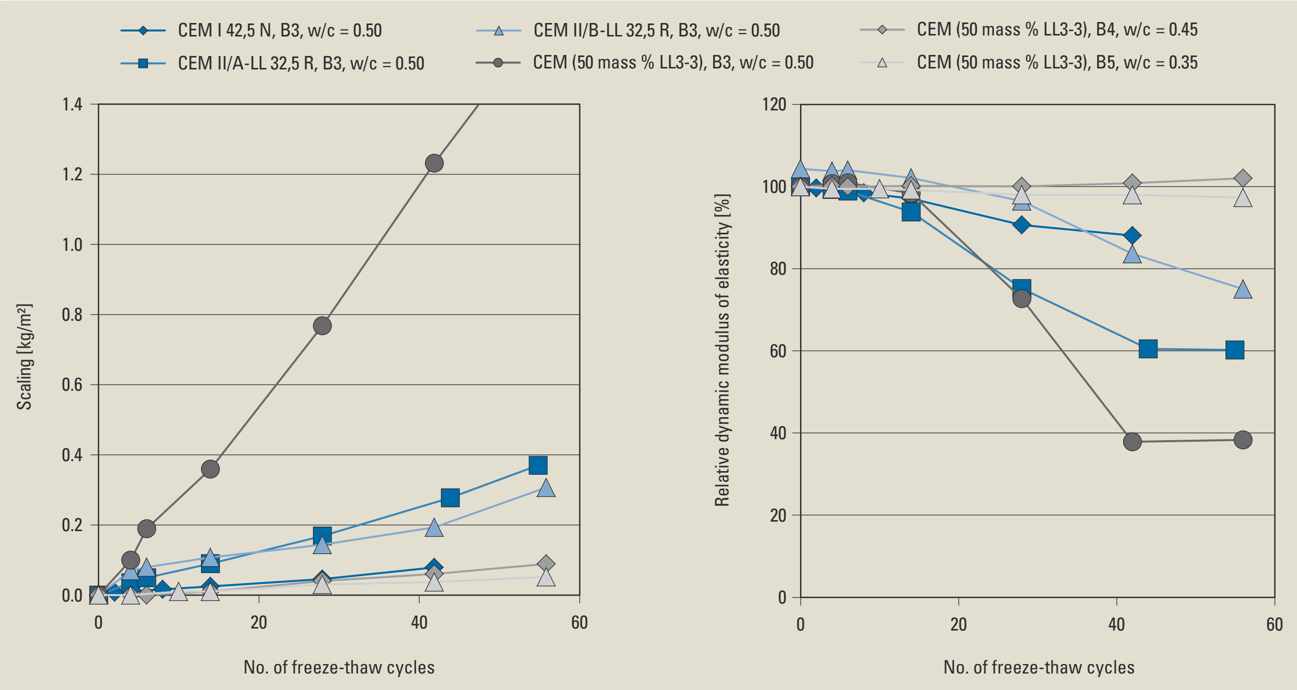


Figure 7: Scaling and relative dynamic modulus of elasticity of concretes B3, B4 and B5 made with cements containing 50 mass % LL3-3

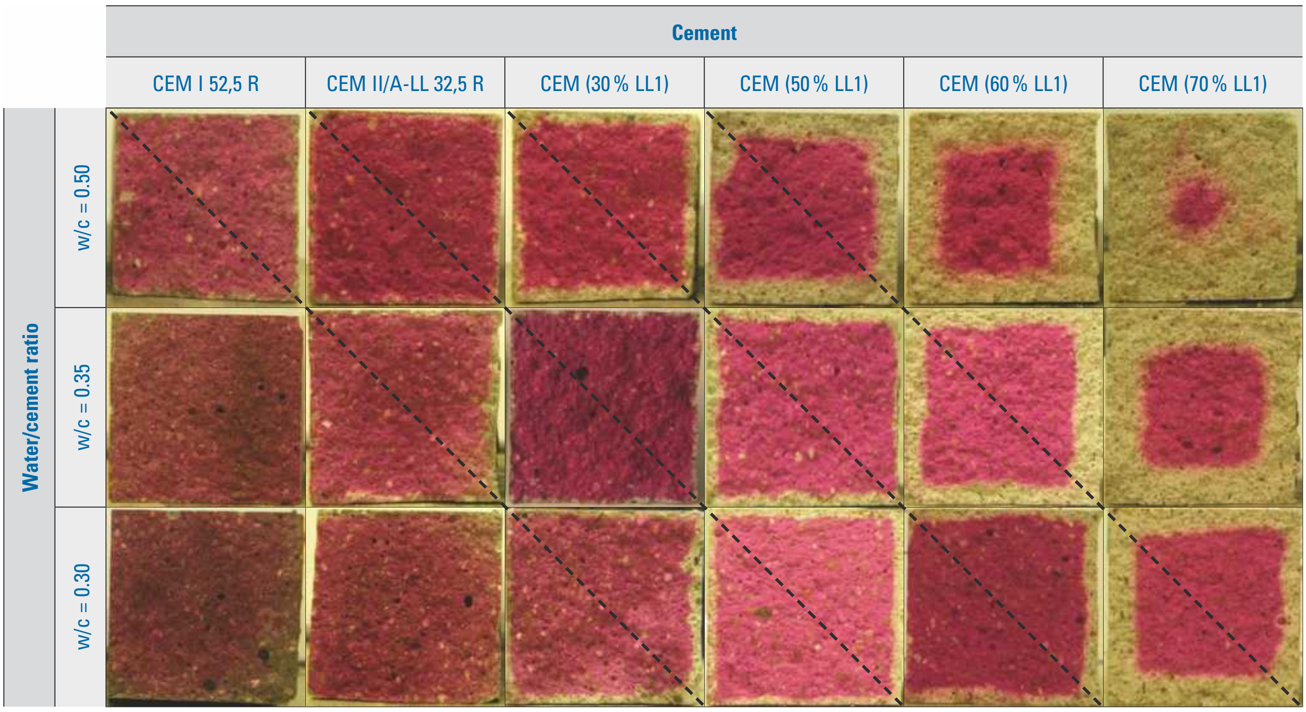


Figure 8: Carbonation of the mortar samples after 140 d

- - - - equivalent depths of carbonation fore also necessary to consider the load-dependent and load-independent deformation when using cements with high limestone contents.

## 3 Plant trials with ready-mixed concrete

Trials were carried out at the Niederkassel ready-mixed concrete plant of the Herkules Transportbeton GmbH & Co. KG in order to evaluate the suitability for practical construction work of the concretes investigated on a laboratory scale.

The CEM (50 mass % LL1) cement was produced on an industrial scale at the Spenner cement plant prior to the trials and stored in one of the cement silos at the Niederkassel site. Formwork for an unreinforced wall was set up in the grounds of the Niederkassel plant to observe the workability of the concrete under practical conditions and the long-term development of the hardened concrete properties. The formwork consisted of two parts at right-angles to one another, each with a length of 3.5 m, a height of 1.5 m and a width of 0.2 m.

Three concretes (M1, M2 and M3) were produced in batches of 2 $m^3$ or 3 $m^3$ (➧ Table 3). A PCE-based superplasticizer was added to the concrete mixer (twin-shaft mixer) by an additive pump.

The moisture of the sand was measured continuously at the ready-mixed concrete plant with an ultrasonic probe so that it could be taken into account in the calculation of the amount of fresh water required. The moisture content of the coarser aggregate was assumed to be 1 mass % (M1). A very rainy day was involved so this value was corrected to 2 mass % (2/8 gravel) and 1.6 mass % (8/16) gravel for the M2 and M3 mix formulations. The air temperature during the trials was about 20 °C.

For the M1 mix the aggregate, cement, water and superplasticizer were added simultaneously to the twin-shaft mixer and mixed for two minutes. The concrete was transferred to a ready-mixed concrete vehicle where it was mixed for a few minutes and then tested. Because the assumed moisture content of the aggregate was too low the M1 mix formulation contained too much water and had a significant tendency to segregation (settling of the paste). Unreacted cement was also found in agglomerations with diameters of up to 7 cm. This was due to the excessively short mixing time and the simultaneous addition of all the components to the mixer. The M1 mix was therefore discarded.

The mixing regime for M2 was changed as follows: the assumed moisture content of the aggregate was adjusted and the paste content, and therefore the cement content, were slightly reduced. The cement and aggregate were pre-homogenized briefly in the dry state and mixed for 1 min after addition of the water. The superplasticizer was then added and the mixing was continued for a further 2 min. During the determination of the fresh concrete properties the concrete exhibited significantly less tendency to segregation. The concrete was therefore used for filling the lower half of the test formwork. However, the concrete then exhibited significant segregation during placement in the formwork in that the coarse aggregate settled. In order to avoid this effect the grading curve for M3 was adjusted to the particle size distribution normally used in the plant. There was a corresponding increase in the proportion of sand and a reduction in the proportion of 8/16 gravel (see Table 3). The upper half of the formwork was filled with this concrete. Neither during the testing of the fresh concrete properties nor during the concreting did the concrete exhibit any segregation.

Table 3: Concrete compositions for the plant trials

| | Unit | M1 | M2 | M3 |
|---|---|---|---|---|
| Batch volume | m³ | 2 | 2 | 3 |
| CEM (50 mass % LL1) cement | kg/m³ | 426 | 407 | 407 |
| Sand 0…2 mm | kg/m³ | 535 | 555 | 713 |
| Gravel 2…8 mm | kg/m³ | 475 | 500 | 487 |
| Gravel 8…16 mm | kg/m³ | 825 | 850 | 697 |
| Water[1)] | kg/m³ | 145 | 138.5 | 138 |
| Superplasticizer | kg/m³ | 2.0 | 1.8 | 1.9 |
| w/c ratio | – | 0.34 | 0.34 | 0.34 |

[1)] Mixing water + aggregate moisture

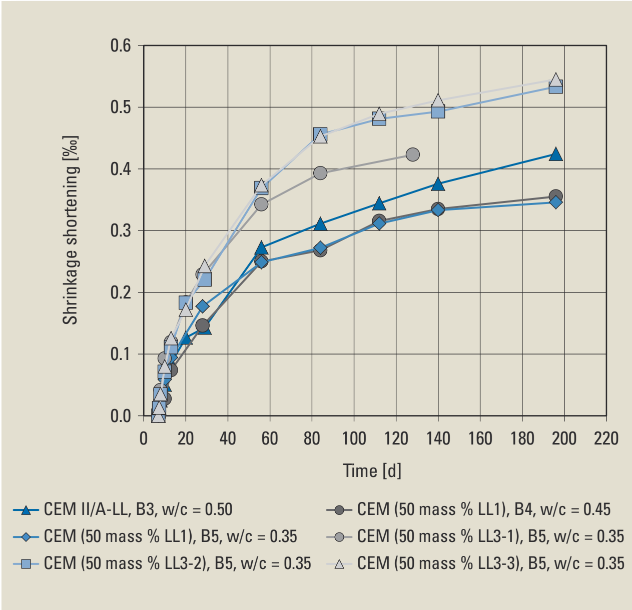


Figure 9: Shrinkage deformation curves

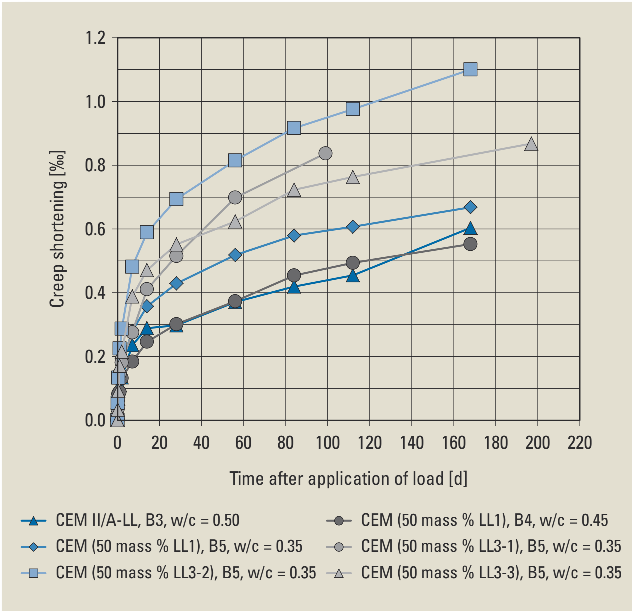


Figure 10: Creep deformation curves

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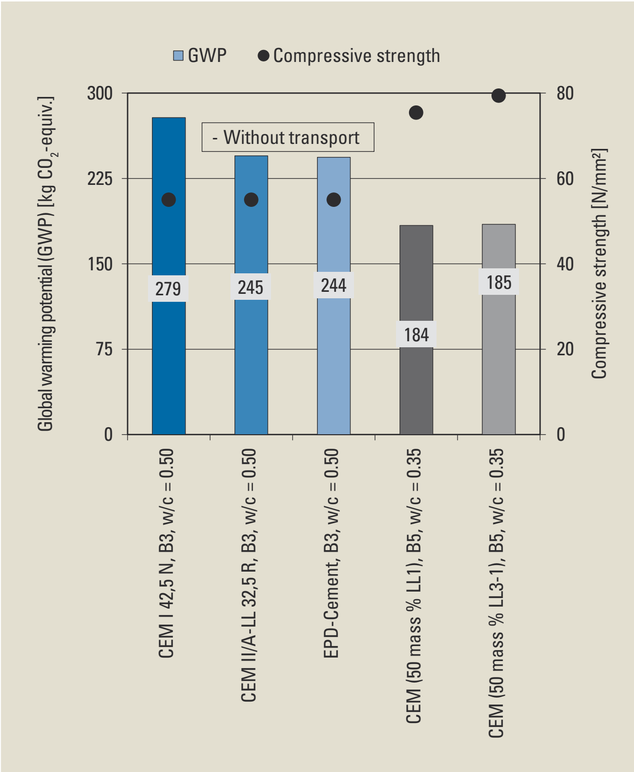


Figure 11: Global warming potential of concretes with a compressive strength of at least 50 N/mm$^2$ and comparable durability in laboratory tests

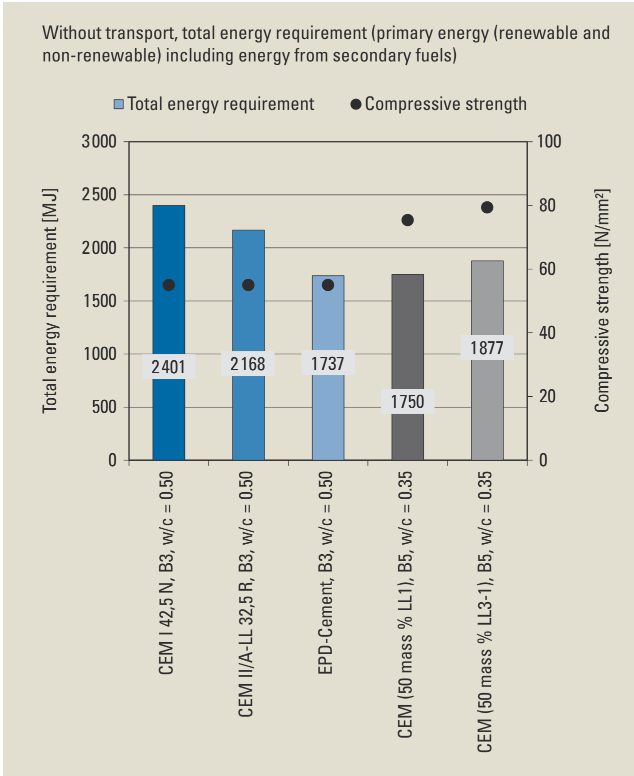


Figure 12: Total energy requirement of concretes with a compressive strength of at least 50 N/mm$^2$ and comparable durability in laboratory tests

Six cubes with edge lengths of 150 mm were produced from each of the M2 and M3 mixes for determining the compressive strength development. The compressive strengths of the two mixes determined from the test cubes were about 22 N/mm$^2$ after one day and about 53 N/mm$^2$ after 28 days, so they were significantly below the values determined in the laboratory trials (>60 N/mm$^2$ after 28 days). The reason for this could have been the weather conditions on that day. It is possible that more moisture was introduced with the aggregate than had been assumed. A water/cement ratio that had been increased in this way would fit with the observed reduction in concrete compressive strengths. This means that particular attention must be paid to the production conditions when converting laboratory results to practical conditions for cements containing high levels of limestone. Greater safety margins (higher cement contents or water/cement ratios that were lowered further than theoretically necessary) would be a possible alternative.

The formwork was stripped from the concrete wall after five days. In the lower part of the wall that had been produced with the coarse-grained M2 concrete some gravel pockets were found in the base area that were attributed to the segregation observed during the concreting. On the other hand, the quality of the surface on the upper part of the wall, which had been made with the finer-grained M3 concrete, was good.

## 4 Evaluating the results with an ecobalance

The reference concretes and test concretes were compared in an ecobalance in order to assess whether the beneficial effects on the results of the ecobalance of the increased use of limestone in the cement are offset by the increased use of cement and superplasticizer in the concrete. The comparison was not carried out between the individual cements but between concretes with the same performance (strength and durability in the laboratory). The ecobalance was drawn up as described in DIN EN ISO 14040 and 14044. The basic data from the GaBi 5 software, the life cycle costs network (cement data project) and the EPD (Environmental Product Declaration) for the German average cement from the VDZ were used for the calculations. The transport distances from the plant to the user were ignored in the evaluation of the concretes. The global warming potential and the total energy consumption as primary energy (renewable and non-renewable), including energy from secondary fuels for concretes containing Portland cement and cements containing varying levels of limestone, are shown in ❱ Figs. 11 and 12.

In the comparison with the concretes made with the VDZ average cement and with CEM II/A-LL 32,5 R cement there was a reduction in the GWP by about 25 % with comparable concrete performance. When compared with the reference concrete made with CEM I cement there was a reduction in the GWP of about 35 %. Because of the significantly greater fineness required for the clinker component (which is hard to grind) in the CEM (50 mass % LL) cements there was no reduction in energy requirement compared with the reference concretes made with the VDZ average cement.

## 5 Final remarks

The results show that cements containing up to 50 mass % limestone are suitable, in principle, for producing structural concretes if the concrete technology is adapted. The concreting trial at the plant showed that a careful adjustment of the water content, the addition of superplasticizer and the aggregate grading curve can produce concrete with good workability on the construction site. In this particular case the strength development was below expectations, which was presumably due to the weather conditions on the day of the test and the requisite increase in water/cement ratio. This means that for cements containing high levels of limestone particular attention must be paid to the production conditions during practical implementation of laboratory results. The laboratory trials with the CEM (50 mass % LL3-3) cement show that care must be taken regarding the interaction of the main cement constituents not only with one another but also, and in particular, with the admixtures. Unplanned introduction of air voids through a superplasticizer can have significantly negative effects on the strength development as well as on the resistance to chloride penetration and carbonation.

The situation can be summarized by stating that sophisticated process engineering measures in the cement plant and equally sophisticated concrete technology measures (low-water concrete with appropriate addition levels of admixtures) in the concrete production would be necessary for the production and use of high-limestone cements (up to 50 mass % limestone). If these measures can be implemented under practical conditions then it will be possible for the concrete to achieve durability parameters that can meet the approval requirements. The robustness of these systems in construction work requires further verification. More attention must be paid to the creep and shrinkage of such concretes and the influence of the limestone quality on the results of freeze-thaw tests also requires further verification. Further results relating to the effects of various influencing factors (fluctuations in the water/cement ratio and in the fresh concrete temperature) are contained in the comprehensive final report on the research project. This can be made available on application to the authors (e.g. sebastian.palm@vdz-online.de).

## Acknowledgement

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