

# THE CARBONATION RESISTANCE OF CONCRETE ON THE BASIS OF BLENDED BINDERS CONTAINING MILLED LIMESTONE

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**ABSTRACT.** The current building industry is essentially changing due to implementation of new approach, which is predominantly motivated by the need to reduce its negative environmental impact. The paper is focused on the experimental evaluation of carbonation resistance in terms of accelerated tests performed on the concrete on the basis of blended binding system incorporating milled limestone. The used commercially produced cement was additionally modified by the limestone powder. The obtained results confirmed, that currently used design standards are convenient to real carbonation process, however further clinker replacement by the milled limestone causes significant loss of the durability of the hardened concrete.

**KEYWORDS:** Concrete carbonation, carbonation front, milled limestone, cement replacement.

## 1. INTRODUCTION

The effort to find out new low-carbon technologies is well visible in all branches of human activities, especially in the industry. It is well visible on the field of new design procedures and predominantly on the field of material engineering. Besides increasing utilization of waste materials to protect non-renewable sources, mostly in Europe is emphasize the implementation of technologies related to lower carbon dioxide emissions. Hence, the environmental trend has been projected to the building industry as well.

Concrete is globally the most used building material, which production is due to content of Portland cement highly energy consuming and related also to enormous emissions of carbon dioxide. It is caused by very high autogenous carbon dioxide emissions during limestone calcination, which is primary raw material for Portland cement production. Approximately 980 kg of CO<sub>2</sub> per a tune of clinker origin during clinker production. The reduction of such an immense CO<sub>2</sub> emissions due to cement utilization is currently solved by two different fundamental ways.

The first is based on the replacement of concrete by the other materials or significant reduction of its volume in the given structure. It is often reached by the application of concrete with increased mechanical and durability performance. The preservation or rather increase of the durability is a crucial aspect of such an approach. The high-performance concrete (HPC) and its material variations were intensively studied during the last decades. The fundamental aspect of HPC is the high-quality binder matrix, which ensures the low permeability of and thus long service-life of the structure. The super resistance of HPC to severe conditions was confirmed by the number of experimental studies [1, 2] and also verified by case studies [3]. The matrix of HPC is based on Portland clinker and other

mineral additives, but due to application of efficient plasticizers it is possible to formulate concrete mixtures with very low water-to-cement ratio ensuring low porosity [4]. The improved properties of used binder suitably allow utilization of aggregate of low quality, although the final durability of the concrete is still higher [5].

The second approach is based on the systematic reduction of Portland clinker amount in the cement and the formulation of new cement types [6], that could be used in case of less demanding application, because traditional Portland cement of often overused, thus is used in cases, where different, low carbon binder, could be successfully applied. This reduction of clinker portion is performed by the replacement of the other cementing material such as fly ash, silica fume, blast furnace slag, etc. Unfortunately, there is enormous lack of cementing mineral additives exhibiting pozzolanic properties, hence the milled limestone is preferably used. CEM II/A-LL or CEM II/B-M are massively applied instead of formerly preferred CEM I or CEM II/B-S during ready mix concrete production. The mechanical properties of these cements are primarily prescribed by the standard [6], however the long-term durability of the concrete incorporating these types of cement incorporating limestone powder is highly questionable. The essential weakness of this mineral additive is its negligible contribution to the cement hydration from the chemical point of view, where it is responsible for the formation of a small amount of monocarbonates [7]. The effect of limestone powder is primarily physical in hydrating paste, where the increased inner surface stimulates formation of new precipitates. Also, standards for concrete production assume limestone powder as an inert additive. Thus, such a formulated binder exhibits higher degree of hydration at the time. Although positive impact

on the paste and concrete rheology, the presence of milled limestone is often responsible for the reduced freeze-thaw resistance and increased permeability [8]. This mineral additive will be widely used in future due to its wide availability and low price, however it is more advantageous to combine milled limestone with active mineral additives such as fly ash, blast furnace slag or calcined clay [9, 10]. Unfortunately, pozzolanic additives are not especially in European union readily available, because the heavy machinery and similar producers of these by products have been removed to other regions during past decades.

## 2. EXPERIMENTAL PROGRAM

The performed experimental program was focused on the evaluation of carbonation resistance of conventional concrete on the basis of blended Portland cement. With respect to the preferable utilization of milled limestone as cement replacement and the technological measure for achievement of good workability of fresh concrete, was part of the above-mentioned cement replaced.

## 3. MATERIALS

The conventional mixture of ready mix concrete C30/37 exhibiting consistency S5 has been designed on the basis of local sources. CEM II/A-LL 42.5 R was selected as main binder material. The aggregate consisted of fine siliceous sand and natural siliceous gravel. The polycarboxylate-based water reducer was complemented with the stabilizing admixture to prevent bleeding. The detailed composition of studied mixtures is shown in Table 1.

Components	LCR	LC15
CEM II/A-LL 42.5 R	320	272
Milled limestone	100	148
Sand 0–4 mm	980	980
Gravel 4–8 mm	260	260
Gravel 8–16 mm	380	380
Plasticizer	2.5	2.5
stabilizer	1.5	1.5
water	175	175
w/b	0.42	0.42

TABLE 1. Composition of studied mixtures.

## 4. PROCEDURES

The mechanical properties of designed concrete mixtures were monitored in time in terms of compressive strength test using cubic specimens of edge 150 mm [11]. The measurement was performed in selected time interval up to 365 days.

The carbonation resistance of the concrete was measured using accelerated carbonation test in accordance with ČSN 13295 [12]. The cubic specimens were after 90 days of curing under humid conditions inserted

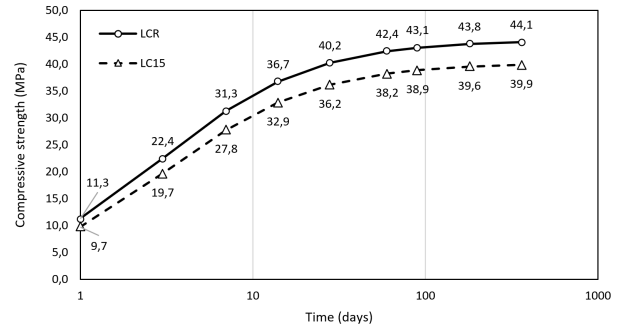


FIGURE 1. Evolution of compressive strength in time.

into the test chamber with 1% CO<sub>2</sub> and RH about 80%. After 56 days are specimens extracted and development of carbonation front is determined using phenolphthalein test, which indicates pH just about 9.5. The carbonation depth was calculated as an average of six measurement on each cube. The process of carbonation in time could be described according Equation 1,

$$d_{carb,field} = K_{field} \cdot \sqrt{t \cdot \gamma} \quad (1)$$

where  $d_{carb,field}$  is carbonation depth (mm),  $\gamma$  is safe factor 1.1,  $K_{field}$  coefficient of carbonation (mm·year<sup>0.5</sup>) and  $t$  is time (years). The coefficient of carbonation could be derived on the basis of accelerated test, which is conducted under specific conditions, by using Equation 2,

$$\frac{K_{acc}}{K_{field}} = \frac{c_{acc}}{c_{field}} \quad (2)$$

where  $K_{acc}$  is coefficient of carbonation obtained during accelerated test with CO<sub>2</sub> concentration  $c_{acc}$  (%), that is often higher than conventional aerial concentration of carbon dioxide  $c_{field}$  (%); 0.03% has been applied. Present calculation was successfully applied in previous research [8, 13].

## 5. RESULTS AND DISCUSSION

The experimental program was focused on the long-term properties of conventional concrete on the basis of blended binder with addition of milled limestone. The complemented part of the campaign was the determination of compressive strength in time during 365 days. The results illustrated in Figure 1 document that after 90 days of curing both studied mixtures fulfilled the requirements of C30/37. On the other hand, using logarithmic scale it is obvious, that long-term gains of compressive strength are after 90 days negligible for these binding systems. That is significant difference in comparison with the strength development is case of binder incorporating active or pozzolanic additives [14, 15].

The calculation of direct environmental savings is usually performed on the basis of reduced carbon dioxide emissions, however it is necessary to take into the consideration also the duration of service-life of

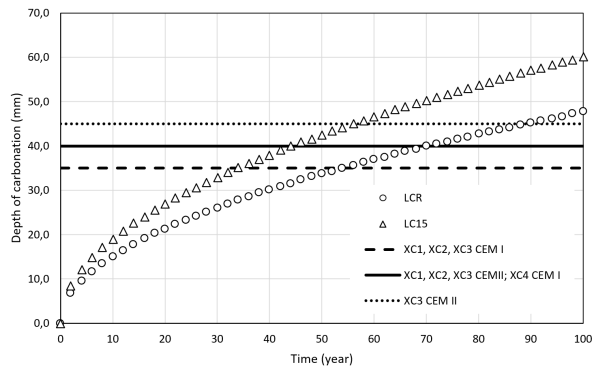


FIGURE 2. Estimation of the progress of carbonation front.

such a structure. Hence, it is crucial to evaluate new technologies in terms of the attained durability. In this experimental program was the process of carbonation applied. Obtained data confirm, that reference mixture, which was modified by milled limestone exhibited slightly lower resistance to the carbonation with respect to used cement, Figure 2. According to applied estimation the carbonation front would pass the concrete cover after approximately 90 years. The second mixture with 15 wt. % replacement by milled limestone exhibited significant decay of the carbonation resistance. The concrete cover would be passed after 55 years, that performs loss of durability performance about 40%. From the other point of view, it is necessary to design thickness of concrete cover 50 mm for LCR and 60 mm for LC15, respectively, for the service life 100 years.

## 6. CONCLUSIONS

The performed experiments confirmed, that mechanical properties of such designed concrete mixtures are nearly similar from this point of view. With respect to the level of cement replacement the differences between single mixtures are negligible. The scope of the program was the evaluation of the resistance of carbonation. The obtained results showed crucially reduced resistance to the carbonation due to additional cement replacement by milled limestone. Just 15% of limestone reduced this durability factor by 40%, thus for similar service life concrete cover would be increased from 50 to 60 mm, what is not feasible with respect to the increased amount of concrete.

It is crucial to note, that reference concrete mixture was based on the CEM II/A-LL cement, where could be the clinker replaced up to 20%. Following cement grade “B”, thus CEM II/B-LL, could exhibit clinker replacement up to 35%. Performed replacement of cement by milled limestone, could be assumed as artificial formulation of CEM II/B-LL in case of the mixture LC15, in addition the extreme level of clinker replacement. Besides negligible differences in mechanical properties, the final service life would be due to 15 wt. % cement replacement reduced from 90

to 55 years. That is why is crucial to take into the consideration the durability of final concrete mixture, not only direct reduction carbon dioxide emission related to the used cement type.

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## REFERENCES

- [1] J. Li, Z. Wu, C. Shi, et al. Durability of ultra-high performance concrete – a review. *Construction and Building Materials* **255**:119296, 2020. <https://doi.org/10.1016/j.conbuildmat.2020.119296>
- [2] M. Amran, S.-S. Huang, A. M. Onaizi, et al. Recent trends in ultra-high performance concrete (UHPC): Current status, challenges, and future prospects. *Construction and Building Materials* **352**:129029, 2022. <https://doi.org/10.1016/j.conbuildmat.2022.129029>
- [3] M. Kynclova, C. Fiala, P. Hajek. High performance concrete as a sustainable material. *International Journal of Sustainable Building Technology and Urban Development* **2**(1):63–68, 2011. <https://doi.org/10.5390/SUSB.2011.2.1.063>
- [4] D. Fan, J. Zhu, M. Fan, et al. Intelligent design and manufacturing of ultra-high performance concrete (UHPC) – a review. *Construction and Building Materials* **385**:131495, 2023. <https://doi.org/10.1016/j.conbuildmat.2023.131495>
- [5] T. Pavlů, K. Fořtová, D. Mariaková, et al. High-performance concrete with fine recycled concrete aggregate: Experimental assessment. *Structural Concrete* **24**(2):1868–1878, 2023. <https://doi.org/10.1002/suco.202200734>
- [6] Cement – Část 1: Složení, specifikace a kritéria shody cementů pro obecné použití [Cement – Part 1: Composition, specifications and conformity criteria for common cements]. Standard, Czech Standard Institute, Prague, 2012.
- [7] A.-M. Poppe, G. De Schutter. Cement hydration in the presence of high filler contents. *Cement and Concrete Research* **35**(12):2290–2299, 2005. <https://doi.org/10.1016/j.cemconres.2005.03.008>
- [8] P. Reiterman, R. Jaskulski, W. Kubissa, et al. Assessment of rational design of self-compacting concrete incorporating fly ash and limestone powder in terms of long-term durability. *Materials* **13**(12):2863, 2020. <https://doi.org/10.3390/ma13122863>
- [9] K. De Weerd, K. Kjellsen, E. Sellevold, H. Justnes. Synergy between fly ash and limestone powder in ternary cements. *Cement and Concrete Composites* **33**(1):30–38, 2011. <https://doi.org/10.1016/j.cemconcomp.2010.09.006>
- [10] I. Bekrine, B. Hilloulin, A. Loukili. Multiscale investigation of cement pastes with low and high-grade calcined clays and slag at early and advanced ages. *Journal of Building Engineering* **78**:107570, 2023. <https://doi.org/10.1016/j.jobbe.2023.107570>

- [11] Zkoušení ztvrdlého betonu – Část 3: Pevnost v tlaku zkušebních těles [Testing hardened concrete – Part 3: Compressive strength of test specimens]. Standard, Czech Standard Institute, Prague, 2009.
- [12] Výrobky a systémy pro ochranu a opravy betonových konstrukcí – zkušební metody – stanovení odolnosti proti karbonataci [Products and systems for the protection and repair of concrete structures – Test methods – Determination of resistance to carbonation]. Standard, Czech Standard Institute, Prague, 2004.
- [13] I. Sáez del Bosque, P. Van den Heede, N. De Belie, et al. Carbonation of concrete with construction and demolition waste based recycled aggregates and cement with recycled content. *Construction and Building Materials* **234**:117336, 2020. <https://doi.org/10.1016/j.conbuildmat.2019.117336>
- [14] N. Singh, P. Kumar, P. Goyal. Reviewing the behaviour of high volume fly ash based self compacting concrete. *Journal of Building Engineering* **26**:100882, 2019. <https://doi.org/10.1016/j.jobee.2019.100882>
- [15] P. Reiterman, O. Holčapek, O. Zobal, M. Keppert. Freeze-thaw resistance of cement screed with various supplementary cementitious materials. *Reviews on Advanced Materials Science* **58**(1):66–74, 2019. <https://doi.org/10.1515/rams-2019-0006>