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Cements with a high limestone content – Mechanical properties, durability and ecological characteristics of the concrete

Sebastian Palm [a], Tilo Proske [b], Moien Rezvani [b,*], Stefan Hainer [c], Christoph Müller [a], Carl-Alexander Graubner [b]

[a] VDZ gGmbH, Tannenstr. 2, 40476 Düsseldorf, Germany
[b] Institut für Massivbau, Technische Universität Darmstadt, Franziska-Braun-Str. 3, 64287 Darmstadt, Germany
[c] Dyckerhoff GmbH, Dyckerhoffstr. 7, 65203 Wiesbaden, Germany

HIGHLIGHTS

- Cements with limestone content up to 50 wt.-% can be used by an adopted concrete technology and reduction of w/c ratio to about 0.35.
- Limestone seems not to be totally inert component. The contribution of limestone to the compressive strength is also remarkable when higher amount of Portland cement clinker is replaced with limestone.
- The production of concretes made of limestone-rich cements exhibited roughly 25% less CO_2 emission, but needs approximately the same energy demand.

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ABSTRACT

This paper deals with the performance of concretes made of cements containing high levels of limestone between 35 and 65 wt.-%. The Article mainly focuses on cements with 50 wt.-% limestone. Several experiments regarding the fresh and hardened concrete properties were carried out. Chloride penetration, freeze-thaw resistance, carbonation resistance and long-term deformation behavior were analyzed.

The results show that concretes with cements containing up to 50 wt.-% limestone and a water/cement-ratio of 0.35 may have sufficient properties for practical application if a stringent supervision is ensured. Furthermore, these concretes can exhibit mechanical and durability properties comparable to concretes according to EN 206-1 and the German national application document DIN 1045-2 made of EN 197-1 cements. Besides, the results revealed that these properties depend highly on the limestone characteristics. Life cycle assessment analysis revealed that a cut-off up to 25% in global warming potential of concretes made with such cements is achievable in comparison with German average cement with the same performance.

1. Introduction

1.1. Motivation

Concrete is known as the most widely used building material of our time. The major environmental impact of concrete comes from the CO_2 emissions during cement production, which is altogether responsible for more than five percent of global anthropogenic CO_2 release. In 2013 more than 4 billion tons of cement were produced and mainly used in the concrete industry [1]. The CO_2 emissions are mainly related to the decalcination of the limestone, the fuel and the electricity consumption [2]. It is visible that the reduction of the Portland cement clinker content in cement will reduce the environmental impact of concrete.

The Portland cement clinker content in cement can be reduced by using supplementary cementitious materials (like ground granulated blast furnace slag (GGBFS) as a latent hydraulic component and fly ash according to DIN EN 197-1 as a pozzolanic component). In addition to the reduction of the environmental impact [3] the mechanical and durability properties can be improved.

Cements with GGBFS are allowed in practice for many decades, e. g. in Germany or the Netherlands. Due to the technical, environmental and the economic benefits, Portland composite cements (CEM II) were developed and increasingly used since early 1990's especially in Europe (see Fig. 1). In Portland composite cements

* Corresponding author.
E-mail address: rezvani@massivbau.tu-darmstadt.de (M. Rezvani).

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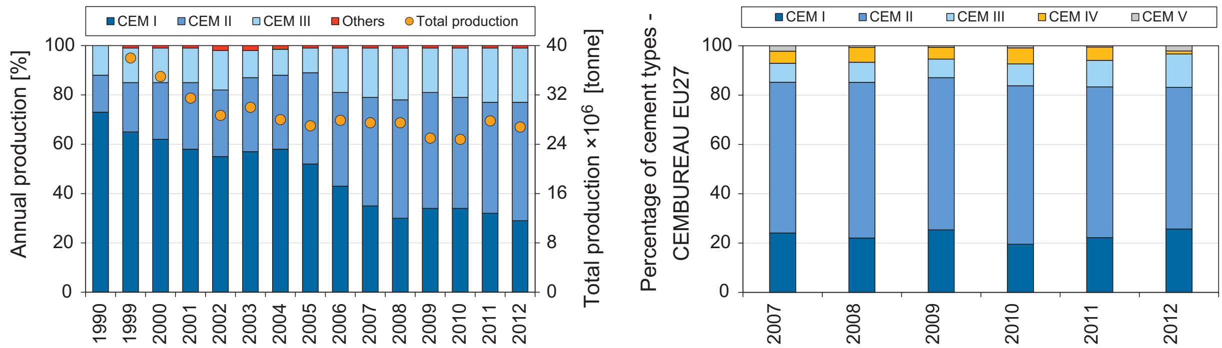

Fig. 1. Annual production of different cement types in Germany (left) [4] and Europe (right) [source: CEMBUREAU data2014].

the clinker is efficiently used together with other main constituents like GGBFS, fly ash, silica fume and limestone to certain ratios. EN 197-1 limits the amount of main constituents besides Portland cement clinker in CEM II cements to maximum value of 35 wt.-%. However, within the last years the production of CEM II cements has reached a constant level, for example in Germany due to the locally limited availability of GGBFS and fly ash (see Fig. 1).

As shown in Fig. 2, the total amount of produced GGBFS and fly ash are nearly completely used by the cement and concrete industry in Germany. This means that an increased use of these constituents in the cement and concrete industry is not probably possible in many countries.

For decades, Portland limestone cement CEM II-LL is used widely in Europe [7] in accordance with the European cement standard EN 197-1. For instance, in year 2012 near 27% of total produced CEM II in Europe were Portland limestone cements (see Fig. 3). The use of cements with a limestone content up to 15 wt.-% is now allowed also in the US and Canada since 2013 and 2008, respectively [8,9]. In Europe, the cement type CEM II/B-LL can even contain limestone up to 35 wt.-%. According to EN 197-1, the total organic carbon (TOC) of LL limestone is limited to 0.2 wt.-%, and the content of clay minerals (obtained from methylene blue test) in limestone must not exceed 1.2 wt.-%. The $CaCO_3$ content of the limestone is not allowed to be lower than 75 wt.-%. However, the use of such cements in concrete is restricted on national levels for severe environmental exposures.

Several efforts by many researchers worldwide have been carried out to develop cements which are not based on Portland cement clinker anymore [10–15]. Many of these solutions could have considerable environmental benefits. However, for the time being either their technical suitability or their economic value and the availability of the constituents are often not verified. Therefore, the efficient use of Portland cement clinker in cement with an increased content of e.g. limestone is worth to be further investigated and developed.

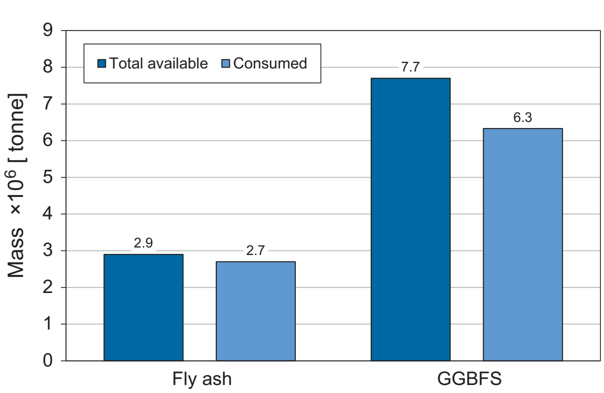

Fig. 2. Annual production and consumption of fly ash and GGBFS in Germany [5,6].

1.2. Concrete with Portland limestone cement

Mechanical performance and durability of concrete made of Portland limestone cement with up to 20 wt.-% limestone are already investigated in depth, e.g. [16–21]. Although limestone is usually considered as an inert component (e.g. [16]), it may influence the microstructure positively and improve the mechanical properties as well as the durability of concrete [16,22–25]. Voglis et al. [22] observed that presence of limestone in Portland limestone cement paste increases the early strength due to formation of tricalcium aluminum carbonate hydrates ($3CaO.Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$). Stark et al. [26] reported that addition of 6 wt.-% of limestone influences the reaction products of C_3S, C_3A and C_4AF which affects the early strength of cement up to four days. Lothenbach et al. indicated that addition of finely ground calcite can accelerate the hydration slightly by providing more surfaces for nucleation and hydration products [24]. A similar conclusion was also made by Proske et al. when using very fine limestone fillers with a Blaine specific surface area of about 16,000 cm^2/g [27]. As a result of the aforementioned alterations of the microstructure, a certain amount of limestone may contribute to the development of the compressive strength [28–31].

The durability of concrete with Portland limestone cement with up to 20 wt.-% limestone against freeze-thaw attack with and without de-icing salts was amply evaluated by several researchers [7,17,32,33]. Most of them found that concrete specimens with Portland limestone cement (CEM II-L and LL) can exhibit more or less the same resistance against freeze-thaw attack in comparison with samples composed with Portland cement. Sprung and Siebel [16] showed a relatively low freeze-thaw resistance of concrete specimens with Portland limestone cement, if the limestone does not meet the requirements of EN 197-1. Schmidt [17] found as well that the influence of the limestone quality on the durability is remarkable.

The carbonation resistance of concrete containing cement with limestone up to 20 wt.-% was reported to be similar to those with Portland cement [34,35]. Schmidt [17] reported that concretes with Portland limestone cement show a slightly higher carbonation depth compared to concretes with Portland cement but they exhibit better resistance against carbonation in comparison with concrete using GGBFS- and fly ash-cements. Barker and Matthews [36] concluded that irrespective for concrete with Portland limestone cement, the carbonation resistance is directly related to the compressive strength. Such behavior was also reported by Hainer [29] and Dhir et al. [37] for cements with up to 50 wt.-% limestone. In similar studies, it was observed that considering the same compressive strength, slightly lower resistance was observed for