Effect of very high limestone content and quality on the sulfate resistance of blended cements

Andre Baldermann [a,1,*], Moien Rezvani [b,1], Tilo Proske [b], Cyrill Grengg [a], Florian Steindl [a], Marlene Sakoparnig [c], Claudia Baldermann [c], Isabel Galan [a], Florian Emmerich [b], Florian Mittermayr [c]

[a] Graz University of Technology, Institute of Applied Geosciences, Rechbauerstraße 12, 8010 Graz, Austria
[b] Technische Universität Darmstadt, Institut für Massivbau, Franziska-Braun-Straße 3, 64287 Darmstadt, Germany
[c] Graz University of Technology, Institute of Technology and Testing of Building Materials, Inffeldgasse 24, 8010 Graz, Austria

HIGHLIGHTS

- Blended cements with limestone replacements up to 65 wt-% were developed.
- Effect of limestone content and quality on blended mortars performance is described.
- Some mixes with ≤50 wt-% limestone substitution performed better than OPC mixes.
- Expansion development is controlled by initial portlandite content and sulfate phase formed.
- Pore structure and carbonate/cement hydrate reactivity influence sulfate resistance.

ARTICLE INFO

ABSTRACT

Sulfate attack was investigated on blended ordinary Portland cement (OPC) based mortars with limestone replacements up to 65 wt-% in 30 g·L^{-1} Na$_2$SO$_4$ solutions at 20 °C and 8 °C for 200 days. Although CEM I 52.5R with ∼12 wt-% C$_3$A was used, some blended mortars with a water/powder ratio of 0.35 and ≤50 wt-% limestone replacement passed the test requirements (Δ-expansion ≤0.5 mm/m after 91 days) and exhibited a better performance than pure OPC reference mixes with water/powder ratios of 0.5 and 0.6. Under accelerated test conditions, the deterioration level of blended mortars arising from sulfate attack can be approximated by the reaction of portlandite with aqueous sulfate to secondary expansive gypsum, ettringite and thaumasite. The pore structure and the reactivity of carbonates and cement hydrates originally present in blended cements should be considered for predicting the long-term stability of concrete in sulfate-loaded environments.

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1. Introduction

1.1. Principles of eco-concretes

The substitution of Portland cement clinker content by supplementary cementitious materials (SCMs) in concrete has become a promising approach both to reduce the global CO$_2$ emission released from the cement industry and to improve the mechanical and durability properties of cementitious materials [1–11]. Due to technical, environmental and economic benefits, SCMs such as ground granulated blast furnace slag (GGBFS), fly ash (FA), silica fume (SF) and limestone are routinely applied in order to produce cements with a reduced Portland cement clinker content, according to EN 197-1. Portland composite cement containing GGBFS and limestone fillers (i.e. CEM II) has been developed in the early 1990′s and is now widely used in many construction sites worldwide. In 2012, ∼27% of the total produced CEM II in Europe was based on Portland limestone cements. The limited availability and the price development of GGBFS and FA in most European countries, however, resulted in an almost constant production level of CEM II-type cement in the last years, i.e. in Germany [3]. The regulations of the EN 197-1 further limit the amount of the main constituents in CEM II to a maximum value of 35 wt-%. Accordingly, the amount of low-cost SCMs such as limestone has been progressively increased in cement mixtures to a maximum value of 35 wt-% in CEM II/B-L and CEM II/B-LL. At the same time, the application of cements with limestone contents up to 15 wt-% has been approved in the US (2013) and in Canada (2008) (ASTM

C595/C595M; CAN/CSA-A3000-08). An efficient use of Portland cement clinker and SCMs and an increase of the limestone content beyond the current limits of EN 197-1 are needed to hold mechanical requirements and to insure environmental benefits of blended cements [3,12–15].

A current technical restriction is the maintenance of water/ powder ratios (hereafter referred to as w/p-ratio) of 0.4–0.6 at limestone contents >20 wt-% in blended cements due to production issues. Therefore, durable concrete made of cement with high limestone contents can only be fabricated if the w/p-ratio is significantly reduced (i.e. to 0.35), as is described in Proske et al. [1]. In this context, the use of a high performance superplasticizer and the optimization of the packing density are efficient measures to increase the workability of blended cements at a reduced water demand and lower Portland cement clinker contents in the cement paste [3,5,14]. In particular, the results of Palm et al. [3] showed that cement-reduced mortars with up to 50 wt-% of limestone substitution and a w/p-ratio of 0.35 exhibit sufficient properties for multifaceted practical application. Corresponding life cycle assessment analysis further suggests that the global warming potential of these mixes can be reduced by up to 25%, compared to the conventional cements according to EN 206-1 and the German national application document DIN 1045-2 made of EN 197-1 cements. Following the concepts described above, blended cements with limestone contents from 35 wt-% up to 65 wt-% have been developed [3]. Their excellent performance in respect to chloride ion penetration, freeze-thaw cycles, carbonation resistance and long-term deformation behavior has already been proven [3,16]. However, to the best of our knowledge no study yet exists, which examines the sulfate resistance of blended cements with limestone powder contents exceeding 35 wt-% (without other reactive SCMs) [17,18]. In this study, the effect of limestone content and limestone quality on controlling the applicability of blended cements with high limestone contents (up to 65 wt-%) in sulfate-loaded environments is elucidated.

1.2. Sulfate attack mechanisms in limestone-rich concretes

Sulfate attack in concrete frequently occurs through interaction of sulfate-bearing solutions with alkali hydroxides, portlandite [Port; $Ca(OH)_2$], calcium silicate hydrates (C-S-H) and calcium aluminate hydrates (AFt and AFm) present in hydrated cementitious materials. The formation of in particular secondary, expansive gypsum [Gp; $CaSO_4 \cdot 2H_2O$], ettringite [Ett; $Ca_3[Al(OH)_6]_2(SO_4)_3 \cdot 24H_2O$] and thaumasite [Tha; $Ca_3(SO_4,CO_3)[Si(OH)_6] \cdot 12H_2O$] often results in severe microstructural damage due to internal stress generation and subsequent weakening of the concrete structure [2,19–29]. The combination of mechanical distress and chemical alteration of the concrete can trigger deterioration of the cementitious matrix of concrete structures within only a few years [30–33].

Fast Gp formation by a through-solution mechanism is frequently observed under conditions used for testing of concrete and mortar in the laboratory, i.e. at temperatures $\geq 20\,^{\circ}C$, alkaline pH and in the presence of highly concentrated Na_2SO_4 solutions [34–36]. However, Gp can also precipitate at $pH \leq 7$ in cracks and in voids close to the concrete surface by the reaction of Port with SO_4^{2-} ions from external sources, i.e. local groundwater and drainage solutions [18,23,37,38]. Secondary Ett typically forms at moderate temperatures ($\geq 15\,^{\circ}C$) and $pH \geq 10.7$, either through direct precipitation from oversaturated pore solutions or by the reaction of aluminate phases (C_3A and C_4AF) and Gp [24,39,40]. Ett formation causes intense cracking and softening of the cement paste by generating expansive crystallization forces especially in the small pores [18,41,42]. Precipitation of Tha occurs at tempera-

tures $\leq 10\,^{\circ}C$ and $pH \sim 9$ in the presence of solutions containing high levels of SO_4^{2-} (up to 30 $g \cdot L^{-1}$), Ca^{2+} and CO_3^{2-} ions and silicic acid [19,22,28,30,43,44].

Current strategies to reduce the harmful effects of sulfate attack on the durability of concrete include, for example, the use of C_3A-free cements (e.g. CEM I SR0, according to EN 197-1) and the addition of GGBFS, metakaolin or FA fillers. These measures results in an increase in the packing density and in a decrease in the permeability of newly developed concrete mixes [2]. Yet, the role of limestone fillers on controlling the sulfate resistance of concrete remains questionable. It is generally accepted that the addition of limestone can enhance the concrete's strength due to improved hydration rates, packing density optimization and the formation of stable calcium carbo-aluminate hydrates [1,5,6,12,45–51]. Recently, Mittermayr et al. [2] showed that the addition of fine limestone powders (up to 35 wt-% substitution for cement) did not increase the expansion of cement-reduced mortars subjected to accelerated sulfate attack, despite of favorable conditions for Tha formation (e.g., $8\,^{\circ}C$ and 30 $g \cdot L^{-1}$ Na_2SO_4 in solution). On the other hand, the use of limestone and dolostone fillers is known to support Tha precipitation in the long-term [18,25,28,30,52,53], suggesting that the rate of Tha formation is significantly lower than that of Gp and Ett [19,22,26,44,54–60]. The present study therefore aims at elucidating the resistance of blended cements containing very high limestone contents (up to 65 wt-% without addition of reactive SCMs) against sulfate attack under accelerated test conditions. The obtained results provide new insights into the processes underlying the formation of secondary, expansive sulfate minerals in limestone-rich cement matrixes.

2. Mix Design, experimental procedure and methods

2.1. Materials and mix design approach

The sulfate resistance of two conventional mortars and of six "blended mortars" was tested by aging standard test specimens either in a 30 $g \cdot L^{-1}$ Na_2SO_4 solution at $20\,^{\circ}C$ and $8\,^{\circ}C$ or in a saturated $Ca(OH)_2$ solution at $20\,^{\circ}C$ for 200 days. The mix design of the mortars is shown in Table 1; important mineralogical and physical properties of the starting materials used are reported in Table 2. In detail, two conventional (reference) mortars were cast using CEM I 52.5R with a clinker content ~ 90 wt-%, C_3A content of ~ 12 wt-% and water/cement-ratios (w/c-ratio) of 0.6 (Ref 1) and 0.5 (Ref 2). The w/c-ratios denote the maximum values allowed for the exposure classes XA1 and XA2, according to the German standard for concrete (DIN EN 206 1/DIN 1045-2), with SO_4^{2-} concentrations in groundwater lower than 600 $mg \cdot L^{-1}$ and 3000 $mg \cdot L^{-1}$, respectively. However, for the exposure class XA2 the use of C_3A-free cement (CEM I SR0 according to 197-1) is stipulated in EN 206-1. For this study, limestone-rich cements were prepared by mixing the same CEM I 52.5R with three different levels of ground limestone type LL1 containing ~ 98 wt-% of calcite [Cal; $CaCO_3$], following the procedure described in [3]. These mortars are labelled as CEM 35% LL1, CEM 50% LL1 and CEM 65% LL1, where the number represents the amount of limestone substitution for CEM I. The effect of the limestone quality on the sulfate resistance of blended cements was tested in a second set of samples, where the substitution of the limestone types LL2-LL4 for CEM I was limited to 50 wt-%. These samples are referred to as CEM 50% LL2, CEM 50% LL3 and CEM 50% LL4. Note here that LL2 and LL3 were taken from the same source and thus they had a similar mineralogical composition, i.e. ~ 77–80 wt-% of Cal, but a different fineness (see Blaine specific surface area in Table 2). LL4 contained ~ 75 wt-% of Cal in addition to minor amounts of dolomite [Dol; $CaMg(CO_3)_2$], quartz [Qz; SiO_2], feldspar and clay minerals. Trace amounts of cement clinker phases in LL4 originate from the grinding of the raw materials in a cement mill. All of the blended mortar specimens were fabricated at a constant w/p-ratio of 0.35 using a polycarboxylate ether-based (PCE) superplasticizer in order to attain a sufficient workability [1] and to maintain a target table flow of 180 mm, according to DIN 1015-3. Blended mortars with higher w/p-ratios (>0.35) and higher limestone contents (>65 wt-% substitution for cement) were not produced due to their notably lower compressive strength, compared to the reference samples made with CEM I and a conventional w/c-ratio (= w/p-ratio) of 0.5 or 0.6. The paste volume of the blended and conventional cements (including standard CEN sand with a maximum grain size of 2 mm) was limited to 420 ± 1 $L \cdot m^{-3}$, in accordance with EN 196-1.