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Alkali-carbonate reaction in concrete and its implications for a high rate of long-term compressive strength increase

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HIGHLIGHTS

- We studied process of ACR in cement mortar with dolomite aggregate over time.
- We observed high rate of long-term compressive strength increase of the mortar.
- Alterations to the mortar microstructure can be related to the strength increase.
- Formation of a Mg–Si–Al phase improves interlocking between cement and aggregate.
- Formation of secondary calcite increases density of binder along dedolomitised grain.

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ABSTRACT

This paper investigates the process of non-expansive alkali-carbonate reaction (ACR) in mortar prepared with dolomite aggregate with specific regard to the compressive strength increase of the mortar. Progress of ACR was studied for one year using the HIROX optical microscope system, a petrographic microscope, and scanning electron microscopy with X-ray microanalysis (SEM/EDS) at different simulated real and accelerated conditions. As reference a mortar mixture prepared by inert limestone aggregate was used. Compressive and flexural tests were also carried out parallel to the microscopic investigation, after 0, 3 and 6 months of exposure to the above conditions. The results indicate that a considerably higher increase in compressive strength was detected over time for the mortar with dolomite aggregate, compared to the one with limestone aggregate. This can be correlated with time and exposure condition and attributed to alterations to the mortar due to ACR. Better interlocking between the Portland cement binder and the aggregate grains, due to formation of a new Mg–Si–Al phase, and a denser binder along the dedolomitised grains, due to formation of secondary calcite, are isolated as important reasons for the increase in compressive strength.

1. Introduction

In Slovenia the majority of aggregates used for concrete production originate from carbonate rocks, limestone, dolomitic limestone, calcite dolomite and dolomite, according to the classification of rocks given in [1]. Recently [2], we have discovered that when using one particular dolomite aggregate in concrete, the rate of increase in both compressive strength and modus of elasticity is considerably higher over 6 months, compared to concrete made with limestone aggregate, even though the compressive strength of the dolomite rock used was lower and both concretes were otherwise of identical mix design. These differences were attributed to the reaction between the cement binder and the aggregate grains of the dolomite rock, called alkali-carbonate reaction (ACR). Extensive research is available regarding the mechanisms of the reaction [3–9], but to our knowledge deficiencies still exist, i.e. its influence on the mechanical properties and durability of concretes exposed to different environmental conditions. According to Katayama [10], the alkali-aggregate reaction of carbonate rocks can be subdivided into three categories: (1) the ACR of dolomitic limestone that results in dedolomitisation, (2) the ACR of non-dolomitic limestone that produces reaction rims and (3) the alkali-silica reaction (ASR) of various carbonate rocks. Deleterious ACR, which causes progressive deterioration of concrete due to expanding cracks, and has been observed and studied by several authors in the past [5,11–14], is most likely a consequence of cryptocrystalline quartz, which is invisible in thin section microscopy, or clay content [10]. Other forms of ACR – dedolomitisation and the formation of reaction rims – should not be harmful to concrete. However, some carbonate rocks without silica content show significant shrinkage in accelerated laboratory tests [6].

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With the possibility of ACR between aggregate grains and cement binder in mind we selected two carbonate aggregates, one from limestone and one from dolomite rock, to design a concrete mixture resistant to moist flue gases of power plant cooling tower. The temperature of flue gases around 60 °C should be considered in the design process. We therefore exposed samples of each of the two rocks and each of the two mortars prepared with the two different aggregates to simulated real conditions of the flue gasses (water at 60 °C) and accelerated conditions (1 M NaOH at 60 °C and 1 M NaOH at 20 °C) for a 1-year period. According to Milanesi et al. [12] 1 M NaOH solution at around 20 °C alters only rate but not the type of the chemical reactions involved in the ACR. The same concentration of alkaline solution is also used for the RILEM ultra-accelerated mortar-bar tests at 80 °C [15]. As reference conditions exposure of the specimens to water at 20 °C was used. This paper will focus on how time and exposure conditions change the mortars' microstructure, investigating by means of optical microscopy, SEM observation and qualitative SEM–EDS analysis. These observations will be analysed with relation to the flexural and compressive strengths of the mortar bars.

2. Experimental study

2.1. Materials and specimens

The mortar bars were prepared using two different carbonate aggregates, denoted as A and B. Aggregate A is a limestone and aggregate B originates from dolomite rock. The parent rocks of the aggregates have different and independent paleogeographic and tectonic histories. The quarry of aggregate A is paleographically part of the Dinarides, while the quarry of aggregate B paleogeographically and tectonically belongs to the Southern Alps [16].

Aggregate A is middle and upper Paleocene, lower Eocene foraminifera's limestone and is formed with long, thin strata. The thickest bend of this limestone was found between Razdrto and Senožeče [17]. This bend is often used for aggregate quarries. For limestone containing Alveolina and Nummulites foraminifera, grey, brown or grey-brown colour is typical [18]. The water absorption of aggregate A is 0.8%, its density is 2690 kg/m^3 and its compressive and flexural strengths are 185 MPa and 18 MPa, respectively. Aggregate B is lower Triassic age dolomite [19,20]. Triassic age rocks are the most prevalent of all rocks in Slovenia. They originated in the Thetys and consist of small depressions and carbonate platforms [21]. The water absorption of aggregate B is 0.48%, its density is 2850 kg/m^3 and its compressive and flexural strengths are 170 MPa and 9 MPa, respectively. The petrographic examination is presented in Section 3.2 below.

In this study two different mortar mixtures were prepared with an aggregate fraction of 0/4. The first mixture (Mixture A) contains limestone aggregate and the second mixture (Mixture B) contains aggregate from dolomite rock. Grain size distributions of aggregates A and B are given in Fig. 1. The binder used was a CEM I 42.5R (SIST EN 197-1, [22]) cement with a Blain specific surface area of 3760 cm^2/g and density equal to 3.09 g/cm^3. The chemical composition of the two aggregates and cement is given in Table 1. The water-to-cement (W/C) ratio and the aggregate-to-cement ratio of both mortars were 0.45 and 3, respectively. Both the mixing of the mortars and the casting of the mortar bars (40 × 40 × 160 mm^3) were completed according to the procedures given in SIST EN 196-1 [23].

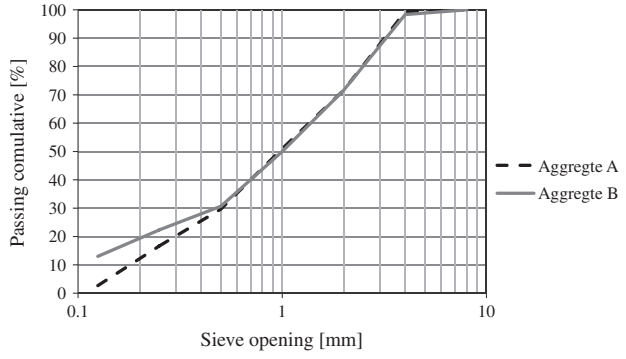


Fig. 1. Grain size distributions of aggregates A and B.

Table 1
Chemical composition of cement and carbonate aggregates.

Oxide (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	Na_2O	K_2O	Cl^-	LOI
Cement	19.33	5.62	2.70	62.06	3.23	2.07	0.35	0.75	0.009	3.70
Limestone	0.06	0	0	55.97	0	0.66	0	0	0	n.d.
Dolomite	0.18	0.07	0.04	31.67	0	19.49	0	0	0	n.d.

n.d. – Not determined.

After casting, the mortar bars were cured in an environment with a relative humidity of 90% and temperature of 20 °C for 28 days. At the age of 28 days the bars were exposed to four exposure conditions: distilled water at 20 °C, 1 M NaOH solution at 20 °C, distilled water at 60 °C and 1 M NaOH solution at 60 °C. The denotations used for the microscopic analyses and mechanical tests carried out after 0, 3, 6 and 12 months of particular exposure are a combination of the aggregate type used (A or B), the solution applied (H2O for water and NH for the NaOH solution), the temperature (20C for the 20° C and 60C for the 60 °C) and the duration of exposure (0m for bars at age of 28 days, and 3m for 3 months, 6m for 6 months and 1y for 1 year of exposure).

The rock sample bars (40 × 40 × 160 mm^3) cut from bigger limestone or dolomite stones were exposed only to 1 M NaOH solution at 20 °C for 9 months.

2.2. Testing methods

For the microscopic observation two different optical microscopes were used. The first was the 3D microscope system HIROX KH 3000, already introduced in [24], with which polished sections and fractured samples were analysed. For the examination of thin sections a polarizing optical microscope with transmitted light, the NIXON Eclipse E 200, was used. Thin sections were made from the mortar and rock bars, in order to identify rock types and reactive minerals, as well as to detect changes in or damage to the microstructure of each material.

A FE-SEM Zeiss Ultra Plus microscope equipped with EDS (Oxford X-Max SDD 50 mm^2 106 detector and INCA 4.14 5 X-ray microanalysis software) was used on polished sections in order to detect the process of dedolomitisation.

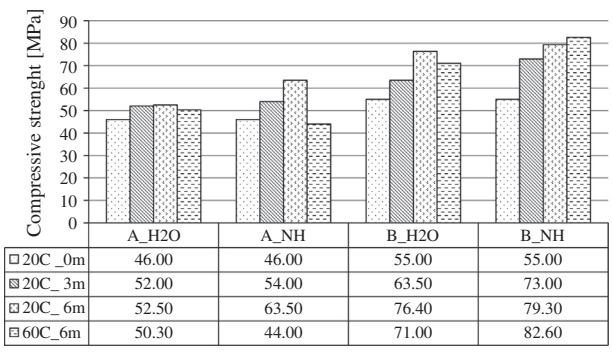
X-ray diffraction analysis was used for the mineralogical detection of carbonate rocks. The X-ray powder data were collected on a PANalytical X'Pert PRO MPD diffractometer with θ–2θ Bragg–Brentano reflection geometry using Cu Kα1 radiation (λ = 1:54059 Å) and with operating conditions of 45 kV and 40 mA.

Flexural and compressive tests of the mortar bars were carried out according to the SIST EN 196-1 standard [23] on 3 and 6 specimens, respectively. Flexural and compressive strengths were determined for each of the different exposure conditions after both 3 and 6 months. As reference values, strengths observed at the age of 28 days, immediately after the curing period, were selected.

3. Results and discussion

3.1. Compressive and flexural strength

Average values observed for compressive strength are presented in Fig. 2 and for flexural strength in Fig. 3. From the compressive strength values in Fig. 2 corresponding to Mixture A, we can see that there is an increase of 13% between the reference value – 46 MPa (A_H2O_20C_0m) – and the value observed after exposure to water at 20 °C for 3 months – 52 MPa (A_H2O_20C_3m). Prolonged exposure (up to 6 months) to the



	A_H2O	A_NH	B_H2O	B_NH
20C _0m	46.00	46.00	55.00	55.00
20C_ 3m	52.00	54.00	63.50	73.00
20C_ 6m	52.50	63.50	76.40	79.30
60C_6m	50.30	44.00	71.00	82.60

Fig. 2. Average compressive strength of the mortar mixtures at selected exposure conditions.