

Long term monitoring of alkali carbonate reactions (ACR)

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Abstract

Throughout the world, carbonate aggregates are one of the most important types of aggregate for the production of Portland cement concrete, which is the single most widely used construction material in the world. This paper presents long time monitoring of progressive alkali carbonate reactions (ACR) in concretes with silica-free dolomite aggregates. Specimens were prepared using four different types of typical Slovenian silica-free carbonate aggregates, which are also commonly found throughout broader Alpine region. All used aggregates were mineralogically pure. Quantitative X-Ray analysis revealed that, on average, dolomite aggregates are composed of ~98 % mineral dolomite. Portland cement CEM I 52.5R, CEM I 42,5 R or CEM III were used as mineral binders. The prepared specimens were submitted to accelerated ageing tests in various environments. The obtained results show that chemical reactions characteristic of the ACR with silica-free dolomite progressed in all aged concrete systems. Additionally, new Mg-Al, Mg-Si and Mg-Al-Si secondary phases were recognized at the aggregate-cement paste interface. Based on observed long-term microstructural and phase changes, it turned out that the soluble Si-source needed for new secondary phases growth did not necessarily originate from the aggregate itself but rather through the Pozzolanic decomposition/regeneration cycle of cement binder. The influence of the progressive ACR on physical and mechanical properties of the cement samples was studied through flexural and compressive strength tests.

Keywords: Alkali carbonate reactions (ACR); dedolomitization; silica-free carbonate aggregate

1. INTRODUCTION

Most of the engineering structures in Slovenia are made of reinforced concrete (RC). Also for the construction of planned new infrastructures, such as the second tube of the motorway tunnel between Austria and Slovenia (crossing the Alpine Karawanks mountain), structures on the new motorway of the so-called third development axis in Slovenia (including 8 bridges, 26 viaducts, 6 tunnels, 4 cut and cover structures) and repository of low- and intermediate-level radioactive waste (LILW repository) in Vrbina (north from Krško nuclear power plant), concrete or reinforced concrete will be used as basic structural material. RC is thus a universally useful material. The composition of concrete mixes in RC depends on local natural resources for the aggregate and cement production. Investigation of the geological map of Slovenia (Figure 1.1) [1] shows that around 45 % of its territory consists of carbonate rocks (limestone and/or dolomites). According to the data of the Slovenian Ministry of Infrastructure for 2018 [2], there were 133 active fields of technical stone (aggregate), out of which as many as 76 extracted dolomite and as many as 28 extracted limestone. This information shows that most of engineering structures in Slovenia use dolomite as aggregate or filler.

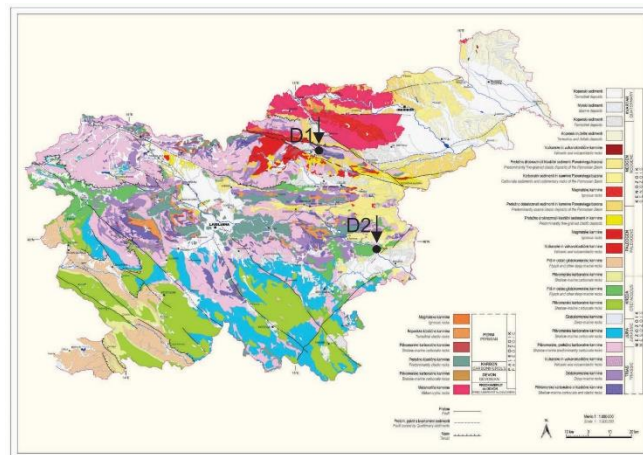


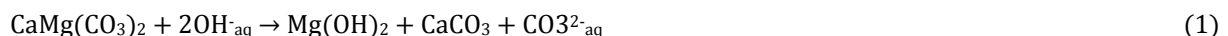
Figure 1.1: The geological map of Slovenia [1] with marked locations of the sources of the tested dolomite aggregates D1 and D2.

It is well known from literature that dolomite aggregate in concretes is not an inert filler, but undergoes various reactions in aged systems. [3-11] The reactivity of carbonate rocks (including dolomite) in concretes has been extensively studied since 1957 when this process was first described in Canada by Swenson [12] and later named the alkali-aggregate reaction (AAR). AAR can be further subdivided into: i) the alkali-carbonate reaction (ACR) and ii) the alkali-silicate reaction (ASR). Among them, the mechanism of deleterious degradation of the dolomitic aggregates has been controversial. Katayama [13,6,7] reviewed published references in this field and deduced that deleterious alkali-silicate gel (ASG) appearance and thus triggered expansion of the dolomitic aggregates is likely due to the ASR of cryptocrystalline quartz within the dolomite aggregates, quite often invisible in thin section microscopy. Formed ASG in humid environment swells and destroys the concrete structure. Because many dolomitic aggregates throughout the world contain considerable amount of reactive silica, progressive ACR in aged concretes with dolomitic aggregates has often been described in combination with the ASR. However, some recent publications shown that ACR in concretes with dolomite aggregates which are completely silica free may also undergo the complete set of individual chemical reactions that are characteristic for the ACR [9,10]. In the proposed mechanism the necessary silicate ions, which took part in the precipitation of some secondary new phases, are supplied from the CSH decomposition/regeneration cycle and the dissolution of C₃A or C₄AF phases in alkaline medium within the cement binder.

Aggregates in Slovenia, which are prone to ASR and thus potentially problematic, are mainly from predominantly silicate rocks containing amorphous SiO₂; i.e. the gravel from the rivers Drava and Mura. Potential reactivity of these gravels is also highlighted in the national addition to the standard SIST EN 206:13 for concrete [14]. On the other hand, a distinctive characteristic of carbonate rocks in the territory of Slovenia, geologically part of Dinaric platform, is extreme mineralogical purity. Slovenian dolomites (rocks) contain almost 98 % of dolomite minerals, while limestones contain almost 98 % of calcite minerals [15]. Nevertheless, our laboratory research recently proved that in an alkaline environment, such as hydrated cement paste (HCP) and limestone binder, Slovenian dolomites are also unstable and susceptible to the ACR [11,8,16]. For this reason, they do not play a role of inert filler inside of concrete.

Considering our recent findings [9], ACR in concretes with silica-free dolomite aggregate is a set of chemical reactions including the process of dedolomitization (Eq. 1), precipitation of secondary calcite (Eq. 2) and formation of some new solid phases, such as hydrotalcite (6MgO·Al₂O₃·CO₂·12H₂O) (Eq. 3), Mg-silicate gel (4MgO·6SiO₂·7H₂O) (Eq. 4) and Mg-Si-Al secondary phases (5MgO·Al₂O₃·3SiO₂·4H₂O) (Eq. 5).

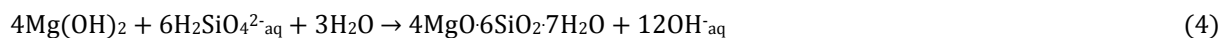
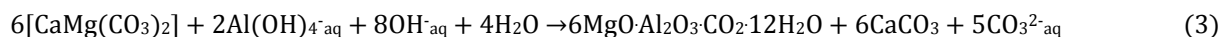
- Dedolomitization



- Formation of secondary CaCO₃:



- Formation of new phases



The above mentioned investigation included accelerated tests, according to the modified instructions from valid norms [17] and recommendations of the technical committees RILEM TC AAR and ACS. As reference, the specimens exposed to distilled water at 20°C were used. We estimated that, with the help of 1M NaOH solution and increased temperature of 60°C, the ACR reactions are accelerated by about 40 times if compared to natural environment.

The story about the ACR reaction becomes additionally complicated when »special concretes« are prepared, for example those with the addition of slag. The reason is that during concrete hardening, slag renders adhesive properties [18-20]. In general, concretes with the addition of slag are considered less alkaline than concretes without the addition of slag, which, of course, also affects the progress of the ACR reaction system [21,22]. Despite the fact that slag has long been a commonly used addition to concretes, there are only partial descriptions of the ACR progress in such systems and a detailed reaction mechanism of ACR is not yet available [23-25].

In addition to the above described chemical aspects of progressive ACR, the formation of new phases and thus connected changes of the porosity within aggregate grains and cement binder undoubtedly affects the functional properties of ageing concretes. As a consequence, in-depth knowledge of the sequence and extent of occurrence of new phases during ACR is of key importance for the prediction of concrete durability in real environment and assurance of the long service life of RC infrastructure.

The aim of this work is to properly describe morphological, microstructural, phase and mechanical changes of concretes with silica-free aggregates during the progressive ACR reaction. For this purpose, concretes with Slovenian dolomite aggregate from two quarries are used and submitted to an accelerated dedolomitization reaction at elevated temperatures in highly alkaline media. In view of ongoing and planned big infrastructural projects in Slovenia such study seems to be of prime importance in order to assure an adequate serviceability, safety and durability of planned objects.

2. EXPERIMENTAL STUDY

2.1 Materials and sample preparation

Table 2.1: Chemical composition, specific surface and density of used cements.

Compound	CEM I 52.5R	CEM I 42.5R	CEM III 32.5N
SiO ₂ content / %	19.4	22.2	30.3
Al ₂ O ₃ content / %	4.7	5.5	9.0
Fe ₂ O ₃ content / %	2.9	3.3	1.6
CaO content / %	63.4	60.4	44.8
MgO content / %	1.6	2.5	6.1
Na ₂ O content / %	0.2	0.4	0.3
K ₂ O content / %	0.7	0.8	0.6
SO ₃ content / %	3.5	2.9	2.4
Cl content / %	0.07	/	/
Blaine specific surface / cm ² /g	4756	3716	4680
Density / g/cm ³	3.11	3.05	2.9

In recent years, various carbonate aggregates were tested on ACR, in combination with three different cements, CEM I 52.5R, CEM I 42.5R and blast furnace cement CEM III 32.5N. Among carbonate aggregates two different dolomite aggregates, denoted as D1 and D2, were selected. Some basic properties of the used cements are given in **Erro! A origem da referência não foi encontrada.**

The dolomite aggregate denoted as D1 was a typical Triassic age late diagenetic (1T_1) dolomite with mineralogical composition 97.0% dolomite and 3.0% calcite as determined by quantitative XRD analysis. Water absorption of the D1 dolomite aggregate was 0.48% and its density was 2850 kg/m³. In addition, the second dolomite D2 is a middle age Triassic dolomite (T_{2+3}). Water absorption of the D2 aggregate was 0.8 % and its density was 2810 kg/m³. The result of mineralogical quantitative XRD analysis revealed that the D2 aggregate was composed predominantly of mineral dolomite (98.1%), with minor addition of mineral calcite representing only 1.9%. Maximum aggregate size of the two aggregates was 4 mm, but presence of fine particles below 0.25 mm was higher for the D1 aggregate.

To ensure enough space inside of the available ventilated ovens, mortar bars with dimensions of 40×40×160 were selected for the samples' preparation. Composition of mortar represents mortar part of the concrete with the water-to-cement ratio 0.45. Mixing and casting of the mortars was carried out according to the EN 196-1 standard [26]. After the casting mortar bars were cured in an environment with a relative humidity of 95±5 % and temperature of 20±2 °C for 28 days. Subsequently, the samples were exposed to accelerated ageing conditions. These accelerated ageing tests included submerging the samples into 1M aqueous solution of NaOH at 60 °C or 20 °C. Periodic analyses of aged samples were performed after 28 days, 3 and 6 months and 1 year. The name of the samples is given in Table 2.2.

Table 2.2: Names of samples.

	Cements			Temperature	
	CEM I 42.5R	CEM I 52.5R	CEM III	60°C	20°C
D1_60	x			x	
D1_20	x				x
D2_60		x		x	
D2_20		x			x
D2_CIII_60			x	x	
D2_CIII_20			x		x

2.2 Analytical methods

Microstructural characterizations of samples were performed by means of optical microscopy (Light Microscopy Zeiss LSM 800) as well as scanning electron microscopy (FE-SEM Zeiss Ultra Plus equipped with EDS Oxford X-Max SDD 50 mm² 106 detector and INCA 4.14 5 X-ray microanalysis software). Prior to the microstructure characterisation, thin sections (15-20 μm) were prepared from the cement composite samples in accordance with the descriptions in [27,28]. To better distinguish among various phases present in the samples, back-scattered electrons (BE) were used for SEM imaging.

Compressive (6 parallel samples) and flexural (3 parallel samples) strengths of the mortars were determined according to the standard EN 1015-11 [29], by using testing machines with capacities of 100 kN and 500 kN, respectively.

3. RESULTS AND DISCUSSION

3.1 Optical and electron microscopy

The microstructural observations were conducted on samples aged for six months and one year. The progress of ACR is demonstrated in Figure 3.1. The dedolomitized reaction rims are observed in optical images as an alteration of the original grey colour of the sparite crystals to the brownish appearance of the secondary products. In contrast, changes in the cement binder are observed in images as dark zones close to dedolomitized aggregate grains. Under the SEM, dedolomitization is visible as the characteristic myrmekitic texture surrounding still unreacted dolomite grain core [6] (Figure 3.1)

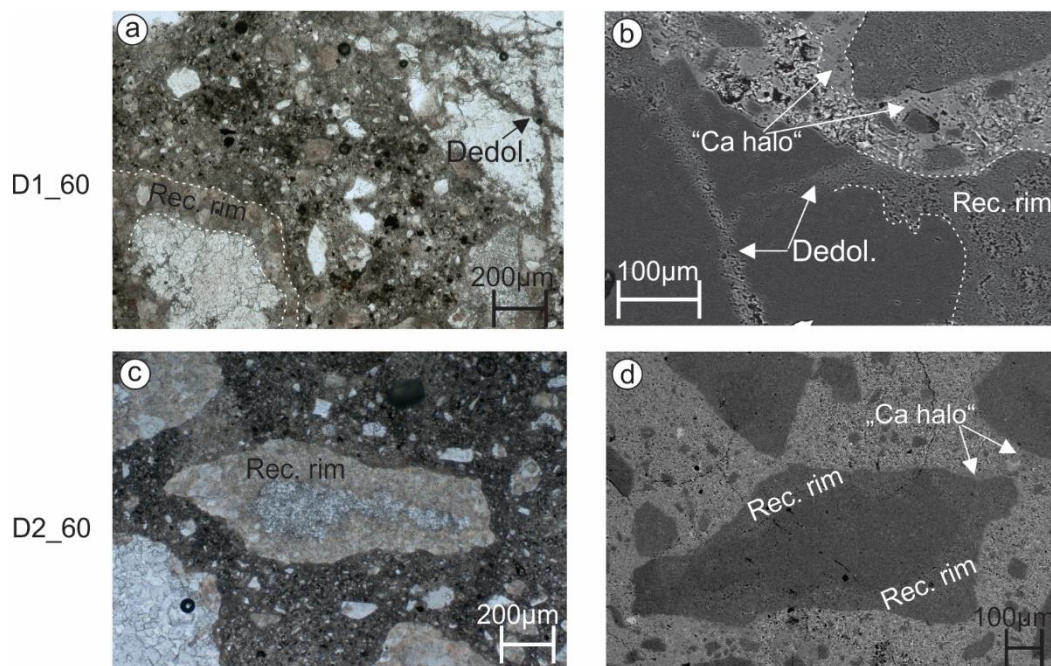


Figure 3.1: Samples D1_60 and D2_60 after 6 months of exposure to accelerated condition. Process of dedolomitization along pre-existing crack (a,b), formation of reaction rim (a b, c, d), and formation of “Ca halo” (b, d) can be observed on the micrographs.

The progressing dedolomitization reaction, as expected, causes the formation of secondary calcium carbonate often named carbonate-halo or “Ca-halo”. The formation of the Ca-halo follows Equation 2 and can be observed in cement paste close to the aggregate/cement phase boundary (Figure 3.1-3.3). The process of dedolomitization is progressive with time and affected by the alkalinity of the cement paste pore water as well as temperature. The results of these relationships are discussed more in details in [9,10]. However, when the dedolomitization rates of two aggregates D1 and D2 are compared, a detailed microscopic observation reveals that dolomite aggregate D1 reacts faster. This phenomenon is probably the consequence of rather different morphological properties of the two aggregates. Namely, the D1 aggregate is richer in fine size-fractions. Consequently, in the D1 – CEM I mortar the specific interface area dolomite aggregate/cement paste is increased, which accelerates the ACR. Furthermore, larger grains of the D1 aggregate contain some pre-existing cracks due to tectonic actions during the rock formation. These pre-existing cracks were subsequently filled with calcite and/or dolomite grains. Widths of the cracks range between a few micrometres to approximately ~50 μm. Through the pre-existing cracks alkaline pore solution is introduced deep inside into the aggregate causing rather faster dedolomitization process. With progress of ACR the Al- or/and Si-involving phases (Figure 3.2) are chronologically formed and follow Equation 3-5.

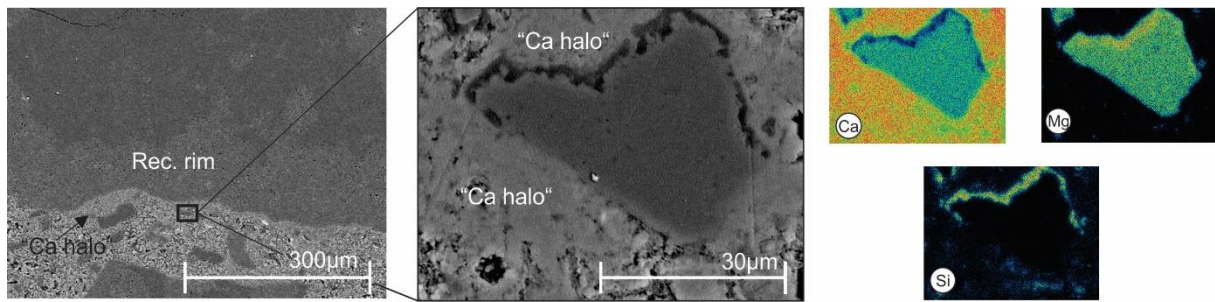


Figure 3.2: Microstructure of sample D2_60 after being exposed for 1 year to accelerated ageing conditions (left). Formation of Mg-Si phase at the aggregate/cement paste interface (middle and right).

If mortar is prepared using aggregate D2 and CEM III (blast furnace slag cement) some significant changes with regards to the D2 CEM I system may be noticed. Most apparently, the dedolomitization process progresses slower with CEM III cement. Furthermore, observed reaction rims do not exhibit unique thickness. Instead, the thickness of the reaction rims seems to be sensitive to the sparite crystal orientation. In addition, some changes in the cement paste at the boundary aggregate/paste are evident and observed in BSE-SEM images as denser pale grey regions (Figure 3.3). To understand these microstructural changes properly, one must consider chemical reactions, which are involved in the ACR process. Basic reactions involved in the ACR system (i.e. dedolomitization and secondary carbonate formation) may be also accompanied by the appearance of some Mg-involving secondary phases. In this view, Mg-Si involving phase is noticed in the aged D2 – CEM III system after 3-6 months and may be understood as a result of the reaction between brucite (from decayed aggregate) and soluble silicate source. Soluble silicate originates from two sources: i) from the cement paste through the decomposition/regeneration of the CSH gel [23-25] and ii) from the slag reaction with alkalis [23-25]. On the other hand, the addition of slag into cement paste seems to prevent formation of Mg-Al gel phase around decaying dolomite aggregates, which is normally found in D2 – CEM I system.

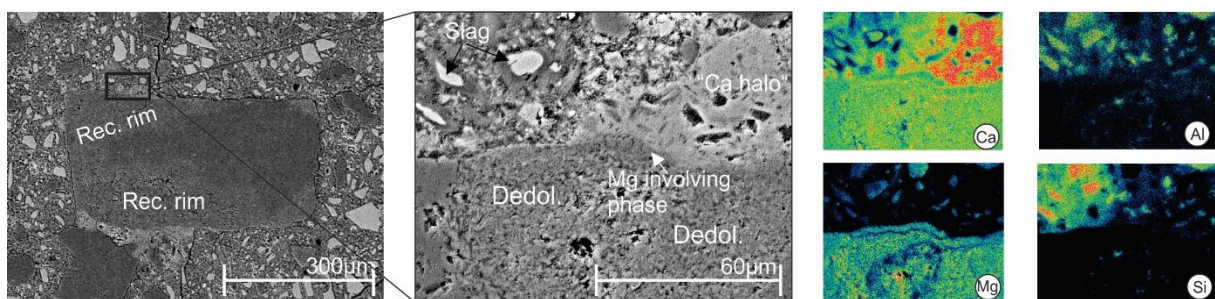


Figure 3.3: Sample D2_CIII_60 after 1 year of accelerated ageing.

3.2 Mechanical properties

Flexural and compressive tests of the mortar bars after various accelerated ageing periods were conducted on 3 and 6 parallel specimens, respectively. Reference mean values of compressive and flexural strengths of the mortars were taken prior to the ageing (ageing time of 0 days).

Results of compressive and flexural tests are given in Figure 3.4 and Figure 3.5, respectively, as mean values after 0, 1 and 6 months, and 1 year of the accelerated ageing at 60 °C (left) and 20 °C (right). It is obvious that the combination of the aggregate D2 and cement CEM I 52.5 resulted in the highest compressive and flexural strength at age of the mortar bars 28 days (start of accelerated ageing). On the other hand, compositions using aggregate D1 and cement CEM I 42.5, and aggregate D2 and cement CEM III, possessed the same compressive and flexural strength at age of 28 days. About 20 MPa higher compressive strength of the specimens D2 with CEM I at age of 28 days is predominantly due to high strength of the cement and partly also due to compact parent rock (without pre-existing tectonic cracks). The same strength of other two compositions is obtained most probably by accident, as combination of lower strength of the aggregate D1 and higher strength of the binder for the D1_60 and D1_20 composition, and higher strength of the aggregate D2 and lower strength of the binder for the D2_CIII composition.

Before discussion of obtained results can be carried out, mechanisms and reaction products responsible for increase as well as decrease of the strength should be introduced. Dedolomitization of aggregate grains increases porosity of the aggregate, due to volume change of -5.1 % [7] and finally result in shrinkage of the cement composite [30]. The first mechanism reduces modulus of elasticity of the aggregate and can potentially also reduce the strength of the mortar. Restrained shrinkage can result in formation of microcracks and with this in the strength reduction. Flexural strength is more sensitive to the presence of higher porosity of the aggregate grains and micro cracks in the mortar, compared to the compressive strength. Formation of secondary calcite in the binder, close to the grains subjected to dedolomitization, decreases porosity of the binder and thus increases its strength and with this also the strength of the mortar as a whole. Formation of hydrotalcite, Mg-silicate gel and/or Mg-Si-Al secondary phases at the aggregate-binder boundary, and for the D1 aggregate also inside of the pre-existing cracks, increase bond strength between aggregate grains and the binder, and bond strength between the micrite base and the sparite cement inside the pre-existing cracks of the D1 aggregate grains. At the macro level this results in increased compressive and flexural strength. Furthermore, we have to also consider the influence of the three different cements used. CEM I 52.5 cement with the highest Blain specific surface area doesn't contribute much to the increase of mortar strength beyond 28 days, while this increase can be important for much coarser CEM I 42.5 cement. Among the three cements, increase in strength beyond 28 days is the highest for the CEM III cement with high content of the GGBFS (Ground granulated blast-furnace slag). Blain specific surface of this cement is approximately the same as for the CEM I 52.5 cement, but the slag grains dissolution in the binder is much slower than for the clinker minerals.

Influence of the accelerated ageing on the compressive strength was the highest for the D1_60 and D1_20 mortar compositions, since increase in the strength after 1 year of the exposure was 30 MPa and 20 MPa at the 60 °C and 20 °C respectively, reaching values of 92 and 83 MPa. For the comparable D2_60 and D2_20 mortars, compressive strength didn't change much during the same time interval. It was sustained around 80 MPa. Difference between the two compositions can be partly due to higher strength increase beyond the 28 days due to the longer hydration of the coarser CEM I 42.5 cement. However, the most important influence can be assigned to different properties of the parent dolomite rocks, more precisely, to the presence of pre-existing cracks in the D1 aggregate grains. For the D1_60 and D1_20 compositions, the process of dedolomitization usually started along these pre-existing cracks, as contact between micrite base and the sparite cement inside the crack is a weak point through which ions from the pore solution can easily enter, allowing fast start of the recrystallization process and formation of Mg-Al, Mg-Si and Mg-Si-Al, also involving phases inside the grains. These phases seem to increase "compactness" of the aggregate grains toward or even beyond that observed for the D2 aggregate, since final strength of the D1_CI mortar is close to that of the D2_CI mortar. The observation is supported by the results of the flexural strength, where D1_60 and D1_20 mortars reached values of 15 and 14 MPa at 60 °C and 20 °C, respectively.

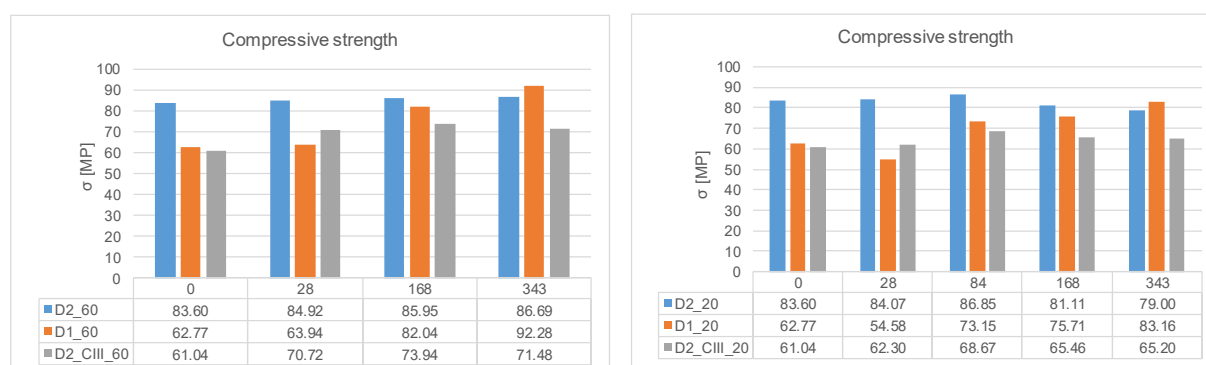


Figure 3.4: Compressive strength of mortar bars.

The most accelerated ageing results of flexural strength at 6 months and 1 year indicate presence of some defects, since there is considerable drop in the strength for the D1_60, D1_20, D2_60 and D2_20 composition. Formation of micro cracks, due to restrained shrinkage in the mortar structure, and increased porosity of the aggregate grains are two mechanisms that can be responsible for the observed behaviour. Shrinkage of cement composites prepared by dolomite aggregate was measured by [30].

Composition with the cement CEM III behaved quite differently. It was confirmed earlier that the ACR in the CEM III binder is much slower than in the CEM I binder. On the other hand, due to slow dissolution of the slag grains (Figure 3.3), resulting reaction products in the binder are formed on very long scale and these products result in higher velocity of the strength increase, as for the D2_60 and D2_20 mortars. Besides, the slag grains can compensate formation of micro cracks or even fill these cracks with the reaction products, as for the most accelerated ageing only D2_CIII_60 mortar didn't face reduction in strength after 1 year.

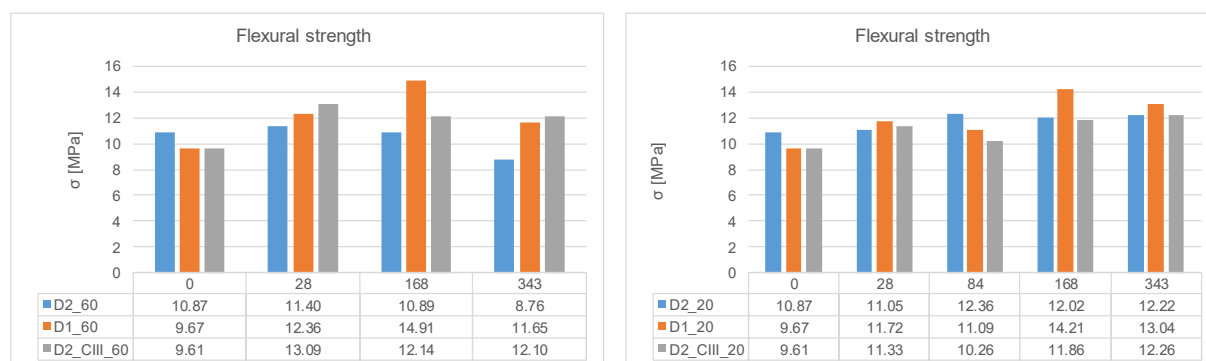


Figure 3.5: Flexural strength of mortar bars.

4. CONCLUSION

This paper assesses non-expansive alkali-carbonate reaction (ACR) in cement mortars prepared with selected silica free dolomite aggregates in its relation to the observed microstructural and mechanical properties. From the obtained results the following major conclusions can be drawn:

1. Dedolomitization, triggered by hydroxyl ions, occurred as a rule within the reaction rims at the outskirts of the decaying aggregate and for the composition using D1 aggregate also along the pre-existing cracks.
2. Dedolomitization is accompanied by Ca-halo formation at the aggregate/binder boundary.
3. In slag free systems the progressing ACR triggers the precipitation of secondary Mg-Si, Mg-Al and/or Mg-Al-Si phases at the aggregate-cement paste interface. The necessary silicate ions are supplied from the CSH decomposition/regeneration cycle while the aluminate ions originate from soluble nature of alumina involving minerals in the cement paste.
4. Slag addition suppresses propagating ACR reaction and prevents formation of Mg-Al gel phase around decaying dolomite aggregates.
5. Gradual appearance of secondary phases during the progressive ACR and resulting increased porosity of the aggregate grains and restrained shrinkage deformations affect mechanical properties of aged cement composites in a way of improving or decaying its mechanical strength.

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