Alkali-dolomite reaction in air lime mortar – implications for increased strength and water resistance

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Abstract

This paper investigates the origin of increased strength and water resistance of air lime mortar prepared by Triassic dolomite aggregate when exposed to humid or wet environments. The mortar specimens were exposed to various ageing conditions and analysed using petrographic and scanning electron microscopy equipped with X-ray microanalysis. Parallel to these analyses, X-ray powder diffraction and strength tests were performed on the specimens. It was revealed that reactions associated with the dedolomitisation process of the dolomite grains in the lime binder (hereafter alkali-carbonate reactions or ACRs) are the source of the improved strength and water resistance. An increasingly alkaline environment accelerated the ACRs substantially. Two parallel processes during the ACRs (dedolomitisation and CaCO_3 dissolution/precipitation) were described in detail. Ageing temperature decisively influenced the kinetics of the dedolomitisation and dictated the path of the CaCO_3 dissolution/precipitation process. After two years of ageing in a water-saturated environment at 60°C, air lime mortar retained a great deal of its initial mechanical strength, and at 20°C its strength was considerably increased. This somewhat unexpected observation was explained as being a result of microstructural changes and/or phase transitions.

Keywords: lime mortar; alkali-carbonate reactions; mechanical properties, CaCO_3 dissolution/precipitation

1 INTRODUCTION

Since the mid-20th century, there has been evidence of the damaging effects of hard and impervious cement mortars that were used in rehabilitation campaigns for historical buildings [1–3]. As a result, lime was rediscovered by European conservation practitioners and has been used as the main binder in restoration mortars since the 1970s [4,5]. Air lime mortars are considered to be the most compatible solution for the repair interventions of historical buildings, seeing as they very often fulfil demand regarding the like-for-like approach, which is a frequently repeated recommendation in conservation practice [6–15]. Among air lime binders,

putties with long slaking periods were recommended first, as they possess improved properties compared to the dry hydrated lime [16,17]. However, due to the limitations of putty lime mortars, especially concerning their durability, and some failed interventions, attention began to shift towards hydraulic limes in the 1990s [5]. These mortars are indeed more resistant to water and frost, and they set and harden much faster than air lime mortars [18–20]. Very recently, concern has been raised by conservation practitioners in the UK that many commercially available natural hydrated limes (NHLs) result in considerably higher long-term strength of repair mortars, compared to their historic counterparts, and they may be too strong for a majority of conservation applications [5]. This is most probably because properties of the NHLs and air lime-pozzolana mortars are evaluated after 28 days, which is the reference age connected with cement-based composites, or possibly also after 90 days, which is a commonly agreed initial age to evaluate the properties of the air lime composites. There are only limited studies in which lime mortars with hydraulic binder were tested at an age older than 90 days, many of which show a decrease in strength of the NHLs and lime-pozzolana mortars at an age beyond 90 days [15,20], or, in contrast, a high increase of the strength with time, which can be harmful to historic fabrics [21].

Although the type of lime binder is the focus for a majority of researchers in the area of historical mortars, characteristics of natural aggregates used for mortar preparation also play a critical role when the performance of lime mortars is described. Aggregate type, grain size distribution, shape of grains, and binder/aggregate ratio are the characteristics addressed when the influence of aggregate is studied [14,19,22–25], but very rarely is the potential reactivity of the aggregate grains considered [22,25,26].

In the Alpine region, many historical buildings were constructed using air lime mortars, with binder and/or aggregate made of local dolomite rocks. When dolomite aggregate is used to prepare the air lime mortar, the alkaline environment may eventually trigger a dedolomitisation process inside the aggregate grains [27–30]. During the dedolomitisation reaction, dolomite crystals in the grains interact with the hydroxide ions that originate from dissolved portlandite in the binder, causing the decomposition of the crystals and the intergrowth of calcite and brucite [25]. Consequently, the carbonate ions are released, and they diffuse into the binder. In the binder, they react with the Ca^{2+} ions that originate from the dissolved portlandite and form secondary CaCO_3 (carbonate halo) around slowly decaying dolomite grains. Dedolomitisation and secondary CaCO_3 precipitation are typically described as alkali carbonate reactions (ACRs) [31]. The ACRs' mechanism in the cement-based systems is nowadays widely accepted, but the literature data on the ACRs in air lime mortars are very limited [30,32–35]. From this perspective, a proper description of ACRs in such systems appears to be rather significant.

In our previous work [25], the reactivity of aggregate, obtained by crushing a particular dolomite rock, inside the air lime binder is reported. The reaction between aggregate grains and binder was observed for up to 6 months of highly accelerated ageing regarding the ACRs (deionised water or 1M NaOH solution at 60°C). A possible increase in water resistance of the air lime mortar, due to the reaction, was detected. This observation was based on results of a parallel study carried out on the air lime mortars using limestone or dolomite aggregate, where the mortar with limestone aggregate was submerged in the solution.

The present study is a continuation of the work reported in [25]. It focusses on the development of the strength and microstructural properties of the same air lime mortar with dolomite aggregate, up to 2 years. A systematic approach and additional analyses enabled a more in-depth description of ACRs in the air lime mortar. Moreover, detected phase transformations were related to the observed gradual development of compressive and flexural strength of the mortars.

2 RESEARCH AIM

Given the absence of systematic studies, regarding ACRs inside pure air lime binder, this paper focuses on a phenomenological description of the ACRs in the air lime mortar with silica-free dolomite aggregates. To accelerate the reactions, exposure conditions selected were deionised water or 1M NaOH solution at 60°C, and 1M NaOH solution at 20°C, even though these conditions are generally detrimental to pure air lime composites. This work aims to clarify the understanding of progressive ACRs and their influence on altered water resistance and mechanical strength, which are the two main issues in restoration and conservation. To the best of our knowledge, detailed phenomenological description of the ACRs is something new, is not found in the majority of published papers [25,36,37], and suggests that the dissolution/precipitation cycle of CaCO_3 is the main cause of the observed improvement of mechanical strength and water resistance of aged lime mortars.

3 MATERIALS AND SAMPLES

The lime mortar mixture was prepared using late diagenetic (Triassic) dolomite aggregate from the northern part of Slovenia and pure lime putty binder. The water absorption of the dolomite aggregate is 0.48% while its density is 2850 kg/m³. Conducted optical microscopy and quantitative X-ray analysis of the aggregate indicate that the main mineral is dolomite. According to quantitative X-ray analysis of the aggregate, dolomite represents ~97% of mineral content, and calcite represents ~3%. The porosity of stone, according to the Terry and Chilingar method [38], is 0.5%.

The binder in the form of lime putty was prepared in a traditional way from soft burnt calcite lime and was aged for more than 1 year. It consists of the minerals portlandite (Ca(OH)_2), calcite (CaCO_3) and brucite (Mg(OH)_2), with the following chemical oxide composition: 86 % CaO, 11.5 % MgO and 1.5 % CO₂. The water content of the putty is 47 %.

The volume ratio between the crushed sand fraction 0/4 and lime putty in the mortar was 3:1. Additional water was needed for the fresh mortar flow value of 13 ± 2 cm (EN 1015-3 [39]), which resulted in the water-to-binder ratio of the mortar equal to 1.62.

Mortar bars (40×40×160 mm) were prepared according to the EN 1015-11 standard [40]. The bars were demoulded after 7 days and put on a supporting system, which allowed uniform access of air to all of the bars' surfaces. Then the bars were kept at laboratory conditions (temperature of 20°C ± 3°C and relative humidity of 60 % ± 5 %) until they reached the age of three months. After that, the mortar bars were exposed to accelerated ageing conditions regarding the reactions of ACRs, simulated by 1 M NaOH aqueous solution at 20°C or 60°C

and deionised water at 60°C. The reference control condition was deionised water at 20°C. These conditions are often used when studying ACRs in cement-based composites [41–43].

The samples were submitted to analyses after various ageing times. The denotation of samples consists of the letters A or B, for the deionised water or the 1 M NaOH solution, respectively, followed by number 20 or 60 for ageing temperature and, finally, the ageing time is given in months (0m, 1m, 3m or 6m) or years (1y or 2y).

4 ANALYTICAL METHODS

Compressive and flexural strengths of the lime mortar were determined according to the standard EN 1015-11 [40], on 3 and 6 parallel specimens respectively, using a Roell-Amsler hydraulic testing machine with the capacity of 100 kN. The testing machine was complemented by load cells with the capacity of 10 kN and 1 kN, adjusted to the compressive and flexural strength of the tested specimens, respectively. Reference values were obtained on three-month-old specimens with denotation of 0m. Following the noting of reference values, tests were carried out after 1, 3, 6 months and 1 and 2 years of exposure to the accelerated or reference ageing conditions. Prior to mechanical testing, the specimens were cooled to 20°C without any drying.

Improved water resistance of the investigated lime mortar was evaluated indirectly through the results of compressive strength tests. Compressive strength values obtained were compared to the compressive strength values of the limestone aggregate air lime mortar that had been exposed to the same accelerated ageing conditions in an earlier study [25].

Microstructure characterisations 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 mortar bars in accordance with the descriptions in [44,45]. To better distinguish various phases present in the samples, back-scattered electrons (BE) were used for SEM imaging. Analyses were carried out after 3 and 6 months, and 2 years of exposure to the accelerated or reference ageing conditions. This paper only presents photomicrographs obtained after 6 months and 2 years. Photomicrographs obtained after 3 months for the accelerated ageing at 60°C can be found in [25].

As a supplementary analysis to identify crystalline phases' development in the aged mortar bars, X-ray powder diffraction (XRD) was carried out on the samples exposed to 6 months of accelerated or reference ageing exposures, with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) in the range 2θ between 20° and 70° using an XPert Pro X-ray diffractometer. A quantitative phase analysis of the samples was done using the Rietveld method.

5 RESULTS AND DISCUSSION

5.1 Compressive and flexural strength

Results regarding compressive and flexural strength are given in Figure 1, as mean value and standard deviation of each combination of exposure time, solution type, and temperature.

Figure 1: Strength of mortar bars: compressive strength (top) and flexural strength (bottom).

The reference mean values of compressive and flexural strengths of the mortar were obtained prior to the exposure to the ageing solutions (ageing time of 0m) as 1.8 MPa (for compressive strength) and 0.62 MPa (for flexural strength).

After exposure to the ageing solution with a temperature of 20°C, both compressive and flexural strength of the lime mortar were maintained at the reference value or increased with the exposure time, up to 2 years. The only exception is the B20 specimen's flexural strength, for which the drop in strength was observed between 1 and 2 years of the exposure. For the A20

specimens, the first increase in the average compressive strength (equal to 50 % compared to the average reference value) was observed after 6 months, following which increases of 60 % and 80 % were observed after 1 and 2 years, respectively. For the B20 specimens, the first 20 % increase in the average compressive strength was measured after 1 month, and after that increases of 80 %, 155 %, 150 %, and 170 % were obtained after 3 and 6 months, and 1 and 2 years, respectively. The increase in the average strength was similar for the flexural load. For the A20 specimens, the observed increase in the average flexural strength was 20 %, 40 % and 50 % after 6 months, and 1 and 2 years, respectively. In case of the B20 specimens, an increase of 25 %, 90 %, 155 %, 215 %, and 135 % was obtained after 1, 3 and 6 months, and 1 and 2 years, respectively.

In [25], we showed that lime mortar with limestone aggregate, but otherwise of the same composition as the dolomite aggregate lime mortar addressed in this study, faced extensive reduction in average compressive strength after 6 months; 60 % (drop from 1.8 to 0.72 MPa) or 66 % (drop from 1.8 to 0.64 MPa) strength reduction in the water or NaOH solution, respectively. Dolomite aggregate lime mortar exposed to the same solutions show (Figure 1) a relatively fast and long-term increase in compressive (and flexural) strength of the mortar. The higher alkalinity of the pore water accelerates the strength increase considerably. These results indirectly demonstrate increased water resistance of the mortar with dolomite aggregate.

Ageing solutions at 60°C, compared to those at 20°C, are increasingly detrimental for the lime mortar. Despite this fact, up to 2 years, all A60 specimens succeeded to maintain compressive and flexural strength close to the initial reference values (0m). For the B60 specimens, the same conclusion can be drawn up to 6 months of the accelerated exposure. However, the B60 specimens were also not completely disintegrated after 2 years, as they had mean compressive and flexural strength of 1.34 MPa and 0.4 MPa, respectively. It is essential to point out that, for the lime mortar where the dolomite aggregate was replaced by the crushed limestone aggregate, extensive weakening of mortar exposed to a solution with 60°C occurs as early as 3 months after starting the accelerated ageing [25]. In the water or NaOH solution, the obtained average compressive strength was 0.27 MPa or 0.19 MPa after 3 months and 0.31 MPa or complete disintegration (0.0 MPa) after 6 months, respectively.

5.2 Mineralogical observations

Typical changes of the lime mortar microstructure, due to the ACRs, were followed by means of the optical and SEM microscopy (Figure 2). With the help of the optical photomicrographs, which focus on a broader area of interest, the advanced dedolomitisation process can be observed at the outer rim of aggregate grains as recrystallisation of the original dolomite crystals to the brownish appearance of the secondary products. More detailed SEM photomicrographs of an area close to the aggregate/lime binder boundary additionally illustrate the ACRs process and enable more precise determination of the dedolomitisation paths and thickness of the recrystallisation rims (details in Figure 2). Ageing media and ageing temperature play an essential role in the dedolomitisation speed. In water at 20°C, only the initiation of dedolomitisation may be observed after 6 months (A20_6m), and more recrystallisation

products are available after 2 years (A20_2y), with the thickness of the recrystallisation rims (hereafter reaction rim) up to $\sim 5\ \mu\text{m}$.

Figure 2: Optical and SEM photomicrographs of the lime mortar aged in NaOH or H₂O solution.

When the ageing temperature is raised to 60°C, dedolomitisation is evident after 6 months (A60_6m). The process starts at the edge of the aggregate grain and continues along the boundary contacts between sparite crystals and/or along pre-existing cracks. After 2 years

(A60_2y), the existence of a so-called “paving structure” is evident in the large aggregate grain (Figure 2f). It is the consequence of dedolomitisation along the boundary contacts and selective progress of the reaction towards the sparite crystals’ centre (some crystals undergo complete recrystallisation, and others are not yet recrystallised). An average thickness of the reaction rims after 6 months and 2 years is estimated to ~5 and ~10 μm , respectively (estimated from optical and SEM images not presented here).

The process of dedolomitisation is even more pronounced if the water is replaced by the NaOH solution. In the NaOH solution at 20°C (sample B20), dedolomitisation may be identified even before 6 months [25], and the formation of a “paving structure” was observed after 6 months. After 2 years (B20_2y), the reaction rims with an average thickness of more than 50 μm are clearly visible. Since the average thickness of reaction rims is larger in the sample B20_2y, compared to the sample A60_2y, it appears that an increasingly alkaline ageing environment (1 M NaOH) accelerates the dedolomitisation process more than the ageing temperature does. If the temperature of the NaOH solution is raised to 60°C (sample B60) the dedolomitisation process starts almost immediately. An average thickness of the reaction rims after 6 months is equal to about 100 μm . After two years, some smaller dolomite grains undergo complete dedolomitisation, and the reaction rims in larger grains are thicker than 200 μm .

SEM/EDS micrographs of samples B20_6m and B60_6m (Figure 3) support the above findings and further reveal the ACRs process in lime mortar, with emphasis on the influence of the accelerated ageing environment temperature. Micrographs of the sample B60_6m (Figures 2g and 3d-f) show that, for the most accelerated ageing, the ACRs process in the lime binder is similar to that observed for the cement binder [41,46,47]. It is characterised by the growth of reaction rims that form via the process described earlier.

Inside the dedolomitised region, dolomite ($\text{MgCa}(\text{CO}_3)_2$) is transformed into poorly soluble brucite ($\text{Mg}(\text{OH})_2$) and calcite (CaCO_3), which appear as alternate layers, forming a pseudomorph structure [31]. The thickness of this pseudomorph structure may not be uniform and depends on dolomite sparite crystals’ orientation (Figures 2e-h and 3d-f). The dedolomitisation process also involves the liberation of CO_3^{2-} ions, which migrate toward the edge of the aggregate grain and into the pores of the surrounding lime binder. The liberated CO_3^{2-} ions react with portlandite ions of the binder and precipitate as CaCO_3 or carbonate halo (hereafter Ca-halo). Formation of the Ca-halo in the lime binder is difficult to follow; however, the Ca-maps in Figure 3 indicate increased Ca-concentration around the dedolomitised aggregate grain.

The ACR process seems to be slightly different if the ageing temperature is lowered to 20°C (Figures 2a-d and 3a-c). The dedolomitised rims are narrower when compared to those forming at the ageing temperature of 60°C, which is an expected consequence of slower dedolomitisation kinetics at lower temperatures. In contrast, slower kinetics make it much easier to observe the nature of the ACRs reactions. It seems that there are preference paths in the dolomite aggregate grain, along the boundary contacts between the dolomite crystals, where dedolomitisation progresses first. These paths extend deep into the grain, as can be observed by the Mg mapping on the Figure 3b and result in the “paving structure” made of yet nonreacted

parts of the grain (Figure 3a). Another, even more distinct observation regarding ACRs at 20°C, is related to the dedolomitised regions that are practically calcite free. According to element maps in Figure 3, the dedolomitised regions contain only Mg-phase (brucite), while the Ca-phase (calcite) must have diffused from the grain into the surrounding binder.

Figure 3: SEM and EDS micrographs after 6 months of the accelerated ageing: a) BSE image of sample B20_6m, b) and c) corresponding Ca and Mg maps, d) BSE image of sample B60_6m, e) and f) corresponding Ca and Mg maps. (brighter and more intense colour corresponds to higher element concentration)

Results of the optical and SEM analyses obtained after 6 months of exposure to the selected ageing environments were complemented by results of the X-ray powder diffraction (Figure 4). Based on the initial lime mortar composition and characteristics of the ACRs revealed in former studies [25,32-34], expected crystalline phases in the aged samples were dolomite (PDF No 000-36-0426), calcite (PDF No 000-05-0586), brucite (PDF No 000-74-2220), and portlandite (PDF No 000-04-0733). From the obtained results (Figure 4), it can be seen that aragonite (PDF No 000-75-2230) was also formed in specimens that were exposed to the solutions at 20°C (A20_6m and B20_6m). Aragonite is considered a less stable polymorph of CaCO_3 , compared to calcite at standard temperature and pressure; however, it often forms first in the CaCO_3 dissolution/precipitation cycle [44,48,49]. In contrast, aragonite was not detected in the A60_6m and B60_6m samples. Since aragonite is not present in the original aggregate grains and thus also not in the non-aged lime mortar, its appearance in the aged A20_6m and B20_6m samples suggest that the ageing temperature at least partially dictates the dedolomitisation process and the crystallised form of CaCO_3 .

According to Table 1, relative contents of the main crystalline phases in the lime mortar vary substantially with the ageing conditions. As expected, dolomite and portlandite progressively vanish during the ongoing ACRs, while brucite and calcite gradually form. Due to the relatively slow dedolomitisation process, the highest dolomite content is present in the A20_6m sample. Additionally, not well-developed dedolomitisation is accompanied by the lowest content of formed brucite and relatively high residue of portlandite. As previously mentioned, the

formation of the aragonite occurs at the ageing temperature of 20°C, with higher content present in the NaOH solution. Relative to the H₂O, NaOH ageing environment at 20°C (B20_6m) accelerates the ACRs process, and consequently decreases the residual dolomite and portlandite contents, and increases the contents of formed brucite and CaCO₃ (as calcite and aragonite form). ACRs are also accelerated by the increase in the ageing solution temperature from 20°C to 60°C. Presented as evidence are increased contents of brucite and calcite, and reduction in the dolomite and portlandite residues. In addition, the Rietveld quantitative phase analysis confirms the earlier observation that an increase in an alkaline environment (1 M NaOH solution) accelerates the ACRs process more than the increased temperature does (Table 1). However, results obtained for the samples A20_6m and A60_6m confirmed that the humid environment and alkaline nature of the air lime binder are sufficient to eventually trigger the ACRs process in lime mortar prepared by reactive dolomite aggregate.

Figure 4: Crystalline phases in non-aged sample and aged samples after 6 months of exposure.

Table 1: Contents of crystalline phases in the samples obtained by the Rietveld method.

	brucite	calcite	dolomite	portlandite	aragonite
Non-aged sample	/	8.8	84.5	6.7	/
A20_6m	3.9	11.5	81.4	2.0	1.2

B20_6m	8.8	20.1	66.8	0.9	3.4
A60_6m	5.1	19.4	74.1	1.4	/
B60_6m	12.3	29.5	57.4	0.8	/

To support the observations about the mechanical and mineralogical properties of the lime mortar exposed to different environments in this study, a phenomenological description of the ACRs' progress in the mortar is given below.

5.3 Phenomenological description of the ACRs progress in lime mortar

To fully understand the observed differences among ACRs' processes in the lime mortar aged in humid conditions at 20°C or 60°C, one must take into consideration some additional facts. In early stages, the concentration of OH^- is relatively high inside the lime binder and relatively low inside the dolomite grains; this means there is a concentration gradient of OH^- ions, which constantly maintains the flow of the ions and subsequently the dedolomitisation process. Additionally, the concentration of $\text{CO}_3^{2-}\text{aq}$ in lime binder remains relatively low for two reasons: i) due to the carbonation process and ii) due to the precipitation of CaCO_3 halo near the lime/dolomite boundary. Therefore, there is also a concentration gradient of $\text{CO}_3^{2-}\text{aq}$ ions, which diffuse in the direction opposite to OH^- ions (from dedolomitised aggregate into lime binder). However, with time, less and less unreacted Ca(OH)_2 (portlandite) is available in the lime binder due to the majority of CaCO_3 halo having already precipitated. When, during late stages, Ca(OH)_2 (portlandite) is more or less all spent, very little $\text{CO}_3^{2-}\text{aq}$ is further consumed in the lime binder. However, due to the alkaline environment, CO_2 absorption from the air remains an ongoing process. These facts lead to a constantly increasing concentration of $\text{CO}_3^{2-}\text{aq}$ in the binder during prolonged ageing. Because CO_2 from the air is absorbed into the alkaline media, it dissolves mostly as $\text{CO}_3^{2-}\text{aq}$ and much less as HCO_3^-aq . With time, the $\text{CO}_3^{2-}\text{aq}$ concentration in the binder should be higher than the $\text{CO}_3^{2-}\text{aq}$ concentration in the decaying aggregate. Additionally, the pH value inside the decaying aggregate is slightly lower than the pH value of the surrounding lime binder, due to OH^- ions being constantly consumed for the continuing dedolomitisation. This pH variation causes the balance between $\text{CO}_3^{2-}\text{aq}$ and HCO_3^-aq inside decaying aggregates to shift slightly toward HCO_3^-aq when compared to the $\text{CO}_3^{2-}\text{aq}$ to HCO_3^-aq balance inside the lime binder. Consequently, the concentration of HCO_3^-aq inside the dedolomitising aggregate is slightly higher than the concentration of HCO_3^-aq inside the binder, while the concentration of $\text{CO}_3^{2-}\text{aq}$ inside the aggregate is slightly lower than the concentration of $\text{CO}_3^{2-}\text{aq}$ inside the binder. The higher concentration of HCO_3^-aq inside the decaying aggregate results in a higher concentration of Ca^{2+} ions. Specifically, $\text{Ca(HCO}_3)_2$ is more soluble than CaCO_3 . Due to the concentration gradient of Ca^{2+} ions between the aggregate and the surrounding binder, Ca^{2+} ions tend to flow from decaying aggregate into the binder. When Ca^{2+} ions diffuse, they reprecipitate as CaCO_3 due to lower concentrations of HCO_3^-aq and higher concentrations of $\text{CO}_3^{2-}\text{aq}$ within the binder. Such a mechanism should eventually dissolve/reprecipitate most (or maybe all) of CaCO_3 inside the aggregate as an additional CaCO_3 halo in the aggregate's vicinity.

However, the question regarding observed differences in the dissolution/precipitation of CaCO_3 at 20°C or at 60°C remains. To answer this question one must accept that the above-described mechanism involves two parallel processes: i) the dedolomitisation triggered by OH^- ions and ii) dissolution/precipitation of CaCO_3 due to the $\text{CO}_3^{2-}\text{aq}$ to HCO_3^-aq ratio inside or outside the aggregate. A relatively higher ageing temperature means faster dedolomitisation kinetics [50,51] and less absorbed CO_2 (consequently also less dissolved $\text{CO}_3^{2-}\text{aq}$ or HCO_3^-aq). Consequently, dedolomitisation overtakes CaCO_3 dissolution/precipitation. On the contrary, lower temperature means more absorbed CO_2 (resulting in more dissolved $\text{CO}_3^{2-}\text{aq}$ or HCO_3^-aq) and slower dedolomitisation; thus, CaCO_3 dissolution/precipitation overtakes dedolomitisation.

Another question addresses the crystalline structure of the reprecipitated CaCO_3 after the dissolution/precipitation process. At first glance, the aragonite appearance during ageing at 20°C seems surprising since, in the presence of ageing conditions, the calcite structure is a thermodynamically more stable CaCO_3 crystalline form. However, under certain conditions of CaCO_3 precipitation, the crystallisation of calcite is somehow discouraged, and aragonite will form instead. More precisely, the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the crystallising fluid, the supersaturation degree, and the time of crystallisation are decidedly important factors but there may also be others. According to literature, increasing concentration of Mg^{2+} ions in the crystallising fluid will cause a concurrent nucleation of calcite and aragonite above the critical supersaturation [52]. The appearance of aragonite is a consequence of increased solubility and, especially, the increased surface energy of calcite when it incorporates Mg^{2+} ions during precipitation. In contrast, the effect of Mg^{2+} incorporation on the aragonite surface energy is much less pronounced. For this reason, with the increased $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the crystallising fluid, the calcite nucleation rate is reduced while the aragonite nucleation rate may not be very much affected, making it favourable at relatively high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios.

Regarding the aged systems, the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the crystallising fluid is predominantly affected by the ageing temperature. Specifically, dolomite solubility decreases with increasing temperature [53], meaning that at 20°C the $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in the crystallising fluid is higher than at 60°C . Such conditions allow the parallel nucleation of aragonite and calcite. Aragonite at 20°C precipitates as needle-like crystals inside the pores of lime binder in the vicinity of the aggregate/binder boundary (Figure 5).

Figure 5: BSC images of B20_6m sample showing aragonite precipitation in the vicinity of aggregate/binder boundary

5.4 Mechanisms responsible for increased strength and water resistance

The phenomenological description of the ACRs progress in air lime mortar with crushed dolomite aggregate, supported by the results of mineralogical analyses, revealed the plausible source of the increased strength and water resistance for the lime mortars. Namely, secondary CaCO_3 in the form of calcite or aragonite that precipitates inside of the lime binder reduces its porosity and thus increases its strength. Two different mechanisms are responsible for the secondary CaCO_3 formation at 20°C:

- 1) CO_3^{2-} ions that liberate during the dedolomitisation process migrate towards the lime binder, where they react with the Ca^{2+} ions of the portlandite and precipitate as CaCO_3 .
- 2) Ca-phase (calcite) that forms during the dedolomitisation process dissolves/reprecipitates from the aggregate grain into the lime binder.

The second mechanism of the ACRs is most likely responsible for considerable increases of the compressive and flexural strength of the lime mortar bars in solutions at 20°C. Although much higher strengths were obtained in the NaOH solution, due to the accelerated dedolomitisation, ACR-induced increase of the lime mortar strength in an aqueous environment should also be considered. However, when studying the progress of ACRs on the micro-level, microstructural changes of mortars aged in water are rather minor and after 2 years much less evident than in the NaOH solution after 6 months (Figure 2). Since the same mechanisms of ACRs were proposed in both environments, accelerated ageing in the NaOH solution seems to be an adequate approach when studying the influence of the dolomite aggregates on the lime mortar microstructural changes.

When the lime mortar is exposed to an ageing solution at 60°C, chemical reactions connected to the dedolomitisation are modified. The main microstructural difference observed in samples aged at 20°C or 60°C is the formation of compact reaction rims composed of brucite and calcite in the case of the higher temperature (Figure 2). Based on this observation, we can conclude that despite faster dedolomitisation at 60°C, less Ca-phase (calcite) dissolves/reprecipitates from the dolomite grains into the lime binder and thus the porosity of the binder does not decrease to such an extent as for the 20°C solutions. As a result, lower strengths were measured for specimens aged in solutions at 60°C.

In order to explain measured drops in strengths (Figure 1), a detailed study of the lime binder itself should be done. Ageing solutions in this study were used, since they accelerate dedolomitisation of the aggregate and thus also associated reactions (ACRs). However, portlandite and precipitated calcium carbonate in the lime binder are also affected by these solutions. This aspect was not a subject of our study, but several authors deal with an influence of temperature, alkalinity and time on the morphology of portlandite and/or precipitated calcium carbonate [54–60]. From these studies, we can conclude that the above-mentioned parameters can change the crystal orientation, particle size, and shape of non-reacted portlandite, and at the same time have a significant effect on the average particle size, specific surface area and morphology of calcium carbonate that precipitates in the mortar. The way the ageing solutions influence the behaviour of the lime binder can be deduced by using the results of our previous study [25]. In this study, properties of limestone aggregate lime mortar were

also analysed. This aggregate is stable in the alkaline environment [41, 45]. Shrinkage of the mortar bars with the limestone aggregate was relatively high in the 1M NaOH solution at 20°C, while the mass of the bars did not change significantly with time. It seems that alkali Na^+ ions influence the volume stability of the lime binder in the mortar. In other three solutions, the mass of the limestone aggregate mortar bars was reduced with time, which indicates leaching of the binder. Drops in the mortar's strength can be due to crack formation and/or leaching. The reduction in strength for the specimens B20 and B60 (Figure 1) is thus most probably mainly due to differential shrinkage inside of the mortar bars and to some extent also the result of leaching.

6 CONCLUSIONS

The reactions associated with the dedolomitisation of Triassic dolomite aggregate grains inside the air lime mortar (ACRs) were monitored for 2 years using petrographic and scanning electron microscopy equipped with X-ray microanalysis. Parallel to these tests, X-ray powder diffraction and compressive and flexural tests of the lime mortar were performed. To accelerate the studied reactions, the specimens were exposed to 1M NaOH or deionised water solution, at 20°C or 60°C. The obtained results enable drawing the following main conclusions:

- An environment that enables the accelerated ageing of the air lime mortar using various temperatures (20°C or 60°C) of the solution modifies chemical reactions attributed to the dedolomitisation process inside the lime mortar.
- Compared to an H_2O environment, a more alkaline medium achieved by the NaOH solution accelerates the observed ACRs substantially. Therefore, only the increased alkalinity of the solution should be used to accelerate the ageing of specimens, when studying the influence of the ACRs on the properties of air lime mortar.
- The ACRs inside the air lime mortar increase its strength and resistance to water, by the formation of secondary CaCO_3 that fills pores inside the lime binder. Secondary CaCO_3 is formed by two reactions. The first reaction is a consequence of CO_3^{2-} ions' liberation during the dedolomitisation process and their migration to the lime binder, where they react with the Ca^{2+} ions of the portlandite. This reaction consumes portlandite and enables the relatively fast formation of secondary calcite in a humid environment. The second reaction is connected to the dissolution/precipitation cycle of CaCO_3 , which forms during the dedolomitisation process inside the dolomite aggregate grain, due to the CO_3^{2-} to HCO_3^- gradients inside or outside the aggregate. This additional CaCO_3 further decreases the lime binder's porosity.
- The two parallel processes during the ACRs, dedolomitisation and CaCO_3 dissolution/precipitation, are the source of the improved strength and water resistance in the lime binder; these are the two main issues in restoration and conservation.

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