

EXPANSIVE MECHANISM OF RILEM AAR-5 CONCRETE MICROBARS WITH DOLOSTONES

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Abstract

Five dolostones composed of dolomites in 10-100 μ m and 0.25-1.42 wt% micro-crystalline quartz were collected and used to prepare RILEM AAR-5 concrete microbars. The concrete microbars were then immersed into 1 mol/L NaOH solutions at 80°C for 200-500 days. The results showed that the concrete microbars expanded at a relative rapid rate during the first 28 days and then gradually slowed down. Expansion of the microbars ranged from 0.16% to 0.35% at 500 days. Reaction rims with 200-500 μ m width were formed. Many micro-cracks were generated and mainly caused by cracked dolostones. A few of micro-cracks developed along the boundary of the dolostones. Alkali-dolomite reaction mainly took place in the reaction rims to form fine calcite and brucite which were mixed together. Dolomite and micro-crystalline quartz outside the reaction rims were not obviously altered. There were calcite-rich zones with a width of 30-100 μ m in the interfacial zones next to dolostones, which formed by a reaction between CO₃²⁻ ions from dedolomitization of dolostones and portlandite from hydration of cements. Micro-crystalline quartz in the reaction rims with 200-500 μ m width was less than 0.5 wt%. Therefore, alkali-silica gels were not obviously observed in the concrete microbars. It was then concluded that alkali-dolomite reaction was responsible for expansion of the RILEM AAR-5 concrete microbars.

KEYWORDS: Dolostones, Concrete microbars, Expansion, Alkali-dolomite reaction

1 INTRODUCTION

Many cases of deterioration of concrete structures prepared with carbonate aggregate were reported in many countries, e.g. USA [1,2], China [3,4] and Canada [5]. The process that lead to concrete deterioration due to the reactivity of carbonate aggregate in concrete was first described in Canada by Swenson [5] in 1957, alkali-dolomite reaction (ADR, termed as alkali-carbonate reaction in some literature) has been studied extensively.

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In alkaline conditions, the dolomite in rocks interacts with the alkali hydroxides from the concrete pore solution to form fine intergrowth of calcite and brucite. This process releases CO_3^{2-} , which migrates to the cement paste and reacts with portlandite to produce calcite.

The mechanism of expansion is still a controversial issue whether alkali-dolomite reaction affects deterioration expansion or not. Katayama et al [6-9] thought that although dedolomitization was observed, the expansion was attributed to the reactivity of cryptocrystalline quartz present in the microstructure of the rocks, which induced alkali-silica reaction (ASR). ASR caused concrete deterioration by silica minerals in the carbonate aggregates. Tang et al. [10-12] proposed that the expansion was caused by ions and water molecules migrating into restricted space and by the growth of brucite crystallized between the reactive layer of calcite and the matrix which formed restricted spaces.

Although expansion of some carbonate aggregates was below the acceptance limit, especially to dolostones, expansion of the concrete microbars increase gradually with curing age and lead to concrete deterioration. In order to simplify study and considering the influence of silica minerals, tests of alkaline reactivity have been conducted on representative samples of pure dolostones aggregates. Expansion of concrete microbars prepared and cured with long-term according to RILEM AAR-5 were measured. Alkali-dolomite reaction was studied by stereomicroscopy, polarizing microscopy, X-ray diffraction (XRD), backscattered electron (BSE) and scanning electron microscopy (SEM).

2 MATERIALS AND METHODS

2.1 Materials

Cement

Portland cement from Jiangnan-Onado Cement Limited Company in Nanjing, China was used. The content of SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , K_2O , Na_2O , SO_3 and loss on ignition in the Portland cement was 19.43wt%, 2.96wt%, 4.73wt%, 64.00wt%, 2.35wt%, 0.68wt%, 0.11wt%, 2.58wt% and 2.81wt%. The alkali content of cement was 0.56wt% $\text{Na}_2\text{O}_{\text{eq}}$.

Dolostones

Five dolostones from Hebei and Jiangxi province of China were used. Table 1 shows the chemical compositions of dolostones. Mineralogical characterization was complemented by ARL X' TRA X-ray diffractometer on natural samples and the acid-insoluble residues, scanning rate was 10° (2 θ) per minute. The content of quartz of natural samples, brucite and calcite in 5-10 mm dolostones soaked in 10% KOH solutions at 150°C were determined by quantitative X-ray diffraction analysis (QXRD), scanning rate was 1° (2 θ) per minute.

Dolostones were mainly composed of dolomite and small amount of quartz. Acid insoluble residues of dolostones DHC and JFG were mainly composed of quartz, illite, clinocllore and plagioclase. Acid insoluble residues of dolostones DHF, DHG and 9# were mainly composed of quartz, as shown in Figure 1.

Grain size of dolomites was measured by laser scanning confocal microscope (LSCM), as shown in Figure 2. Distribution of grains size of dolomites in dolostone JFG, DHC, DHF, DHG and 9# are 10-40 μm , 10-40 μm , 40-400 μm , 40-200 μm and 30-100 μm , respectively.

Content of acid insoluble residues and quartz in rocks was given in Table 2. Dolostones JFG, DHC, DHF, DHG and 9# contained 1.55wt%, 1.94wt%, 2.61wt%, 0.89wt% and 0.87wt% acid

insoluble residues, respectively. Dolostones JFG, DHC, DHF and DHG contained 0.55 wt%, 0.92 wt%, 1.42 wt% and 0.25 wt% quartz, respectively.

Mortar bars were prepared according to RILEM AAR-2[13]. Figure 3 shows expansion of RILEM AAR-2 mortar bars prepared with dolostones. Expansions of mortar bars with dolostones JFG, DHC, DHF, DHG and 9# increased with curing age and reached 0.027%, 0.028%, 0.068%, 0.022% and 0.029% at age of 28d. Expansions of mortar bars with dolostones JFG, DHC, DHF and DHG reached 0.042%, 0.043%, 0.083% and 0.039% at age of 182d. These dolostones may be classified as non-reactive because the expansions at 28d or 182d of the mortar bars were all less than 0.10%.

2.2 Methods

Concrete microbars were prepared according to RILEM AAR-5[14]. Alkali content ($\text{Na}_2\text{O}_{\text{eq}}$) of cement was boosted to 1.50% by addition of NaOH in the mixing water. The concrete microbars were cured in 1 mol/L NaOH solutions at 80°C.

3 RESULTS

3.1 Expansion of concrete microbars

Figure 4 shows expansion of RILEM AAR-5 concrete microbars prepared with dolostones. The concrete microbars expanded at a relatively rapid rate during the first 28d and then gradually slowed down. Expansions of concrete microbars with dolostones JFG, DHC, DHF, DHG and 9# increased with curing age and reached 0.083%, 0.094%, 0.066%, 0.078% and 0.071% at age of 28d. Although expansions of the microbars with dolostones were less than 0.10% at age of 28d, they reached 0.126%, 0.119%, 0.192%, 0.102% and 0.237% at age of 210d, expansions of concrete microbars with dolostone DHF reached 0.352% at age of 500d. These results indicate that the dolostones were expansive in alkali solutions.

3.2 Microstructures of concrete microbars

Dolostones aggregates showed the development of a reaction rims in contact with the cement paste. Figure 5 shows alkali-dolomite reaction rims of concrete microbars prepared with dolostone DHF according to RILEM AAR-5 cured at different age. Reaction rims were appeared at local zone, then widened with time gradually and formed continuous rims finally. Width of reaction rims was 100-300 μm at age of 270d.

Alkali-dolomite reaction mainly took place within the reaction rims. When treating with dilute HCl solutions, it was found that dolomites were completely depleted inside the reaction rims and alkali-dolomite reaction gradually took place from edge to interior of dolostones. Figure 6 shows typical cracks patterns of the microbars cured for 440 days. Many cracks were originated from aggregates and extended to pastes, which were empty and were not filled with ASR gel. A few of penetrating cracks were observed (Figure 6 (a)).

The dolostones with size of 5-10mm were soaked in 10% KOH solutions at 150°C for 7d, and developed the same reaction rims as that in concrete microbars. Figure 7 shows XRD patterns of 5-10mm dolostones DHF untreated and soaked in 10wt% KOH solutions at 150°C for 7d. Brucite and calcite were identified inside reaction rims (edge of the 5-10 mm dolostones).

The interface between aggregate and cement paste was shown in Figure 8. The reaction zone was found at the cement paste (defined as the carbonated cement paste zone by petrography). According to the SEM-EDS (Figure 9), a large amount of calcite was observed in the zone. Simultaneously, XRD were also carried out for cement paste, and the results show that there were a mass of calcite in the carbonated cement paste zone, as shown in Figure 10.

The 5-10 mm dolostones were soaked at 150°C in 10 wt% KOH solutions, and there was 0.69 mol/L CO_3^{2-} ions in the solutions after cured for 110h. The results show that dedolomitization of dolostones produced a large amount of CO_3^{2-} ions migrated from dolostones to cement paste and reacts with portlandite to form calcite.

4 DISCUSSION

The content of quartz that may be reacted with alkali solutions is perhaps a key parameter to determine alkali-silica reactivity of rocks. The content of acid insoluble residues and quartz of dolostones studied were less than 3% and 1.5% respectively (Table 2), which seems the influence of ASR would be not considered to discuss the alkali-dolomite reaction in this paper. The results showed that micro-crystalline quartz in the reaction rims with 200- 500 μm width of the RILEM AAR-5 concrete microbars was less than 0.5%. Expansion of RILEM AAR-2 mortar bars prepared with dolostones was all less than 0.10% at age of 28d. When mortar bars cured with long term, Expansions of mortar bars all less than 0.10%. These dolostones may be classified as non-reactive according to RILEM AAR-2.

Many cracks were originated from aggregates and extended to pastes in RILEM AAR-5 concrete microbars, which were empty. ASR gels were not obviously observed in the RILEM AAR-5 concrete microbars. Therefore, expansion of the RILEM AAR-5 concrete microbars cannot be attributed to ASR of the reacted quartz. ADR might play a significantly contributing role in expansion of the concrete microbars. It would be then concluded that alkali-dolomite reaction was responsible for expansion.

Alkali-dolomite reaction produced fine calcite and brucite, which were mixed together. The content of brucite and calcite in 5-10 mm dolostones soaked in 10% KOH solutions at 150°C was determined by QXRD, molar ratio of calcite and brucite was 1:1 as shown in Table 3, indicating that the calcite and brucite were formed in situ. The expansion results from the crystallization pressure caused by the growth of the fine calcite and brucite formed in restrained space, and dedolomitization could directly cause expansion of dolostones.

5 CONCLUSIONS

(1) Alkali-dolomite reaction of dolostones JFG, DHC, DHF, DHG and 9# with less than 0.5wt% reacted quartz in RILEM AAR-5 concrete microbars might play a significantly contributing role in expansion of the concrete microbars. ADR was responsible for expansion in the concrete microbars.

(2) Alkali-dolomite reaction produced fine calcite and brucite in situ, and CO_3^{2-} ions migrating to the interface between the aggregate and paste, reacting with portlandite from the hydration of cement to form calcite crystals. The calcite-rich zones were 30-100 μm width.

(3) Under the attack of alkaline solutions, dolomites were completely depleted from the edge to the core of dolostones, and the reaction rims were developed with 200-500 μm width.

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TABLE 1: Chemical composition of dolostones.

Sample	Chemical composition /wt%						
	LOI	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Total
JFG	45.25	1.00	0.18	0.29	29.64	23.17	99.51
DHC	45.03	1.35	0.13	0.31	29.71	22.46	98.98
DHF	45.75	1.61	0.19	0.29	29.01	22.50	99.35
DHG	45.26	0.29	0.17	0.30	29.99	23.28	99.28
9#	45.94	0.24	0.14	0.26	30.41	21.64	98.63

TABLE 2: Content of acid insoluble residues and quartz in rocks.

Sample	JFG	DHC	DHF	DHG	9#
Acid insoluble residues /wt%	1.55	1.94	2.61	0.89	0.87
Quartz /wt%	0.55	0.92	1.42	0.25	--

TABLE 3: Molar ratio of calcite and brucite.

Time /days	1	4	7	10	14
molar ratio of calcite and brucite	1.17	1.02	0.94	0.96	1.03

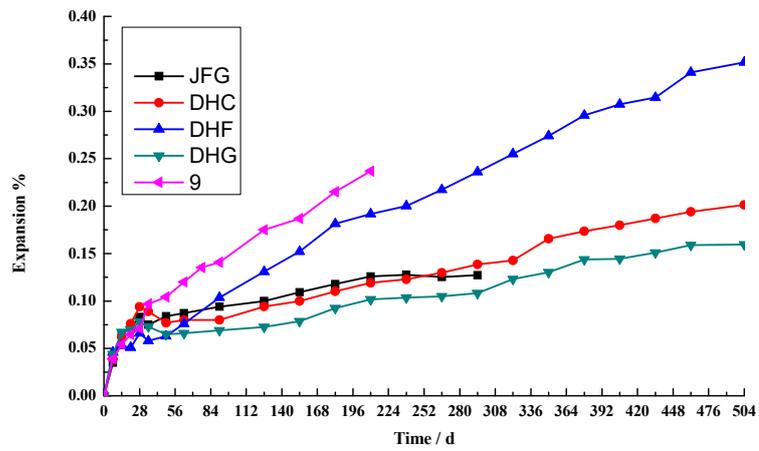


FIGURE 4: Expansions of concrete microbars prepared with dolostones according to RILEM AAR-5

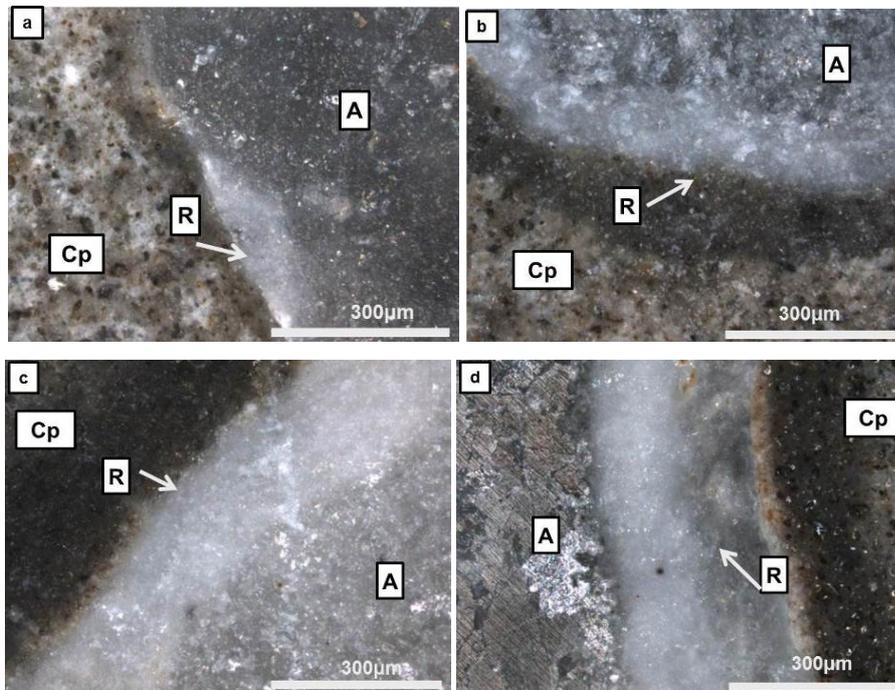


FIGURE 5: Alkali-dolomite reaction rims of concrete microbars prepared with dolostone DHF according to RILEM AAR-5 in different age. (a)- (d) Concrete microbars cured 28d, 90d, 180d and 270d, respectively. A: aggregate, CP: cement paste, R: reaction rims.

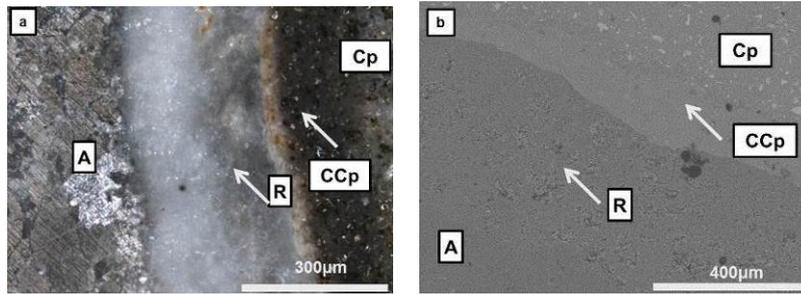


FIGURE 8: Image of interface between aggregate and paste in concrete microbars prepared with dolostone DHF cured for 270d according to RILEM AAR-5. (a) Photomicrograph of stereo microscope, (b) Photomicrograph of BSE. A: aggregate, CP: cement paste, R: reaction rims, CCp: carbonated cement paste zone.

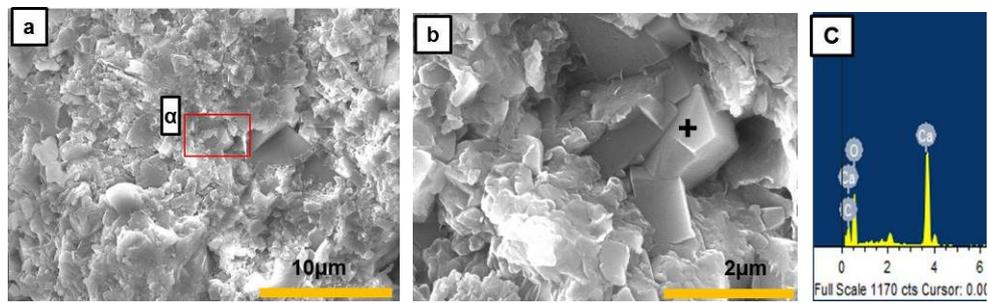


FIGURE 9: Carbonated cement paste zone of concrete microbars cured for 440d. (a) Morphology, (b) Detail of the sector α in Figure 9a, (c) EDS spectra determined in Figure 9b.

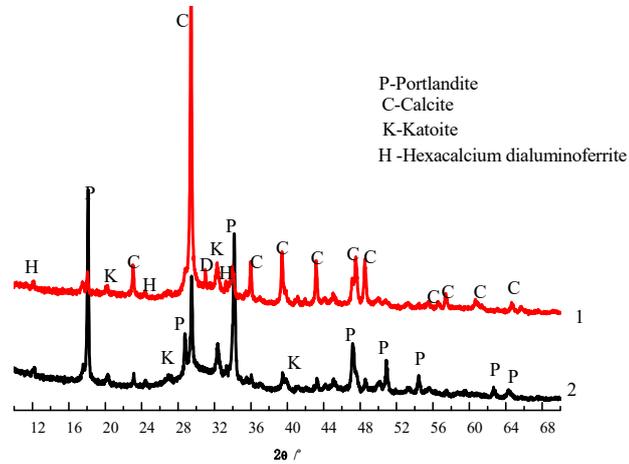


FIGURE 10: XRD patterns of pastes in concrete microbars cured for 440d. 1: cements paste closed to the reaction rims, 2: paste far from the reaction rims.