EXPANDABILITY OF ALKALI-DOLOMITE REACTION IN DOLOMITIC LIMESTONES

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Abstract

Some Ordovician dolomitic limestones with 6vol%-25vol% dolomite in 10-80μm and limestones without dolomite were selected from some quarries of China. Expansion of concrete microbars prepared with the dolomitic limestones and limestones was tested according to RILEM AAR-5. Reactivity of quartz in these rocks was evaluated by quantifying unreacted quartz in aggregates of the concrete microbars and/or in rock powders soaked in 1 mol/l NaOH solutions at 80^{o}C by a selective solution method with phosphoric acid. Reaction products of alkali-silica reaction (ASR) and alkali-dolomite reaction (ADR) were analyzed by X-ray diffraction (XRD) and scanning electron microscope (SEM). Cracking patterns in concrete microbars were investigated by SEM and optical microscope (OM). Results show that expansion of the concrete microbars may be greater than 0.10% when 2.88%-4.36% quartz in limestones was reacted and less than 0.10% when 0.67%-1.62wt% in limestones was reacted. Dolomitic limestones in which 0.06%-0.99% quartz was reacted might bring about the concrete microbars to expand greater than 0.10%. Dolomite in the dolomitic limestones was reacted to form calcite and brucite and no obvious alkali-silica gels were detected. Cracks in the concrete microbars were almost empty and originated mainly from dolomite-rich zones of dolomitic limestone aggregates into cement pastes. Therefore, it is deduced that ADR of dolomitic limestones may contribute expansion to the concrete microbars.

Keywords: dolomitic limestone, dolomite, quartz, expandability, alkali-dolomite reaction

1. INTRODUCTION

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Swenson [1] in 1957 found that a dolomitic limestone coarse aggregate produced excessive expansion in field concrete and laboratory concrete prisms in a few weeks. However, ASTM mortar bar test failed to detect its alkali-silica reactivity. Hadley [2] pointed that although some of the dolomitic limestones tested contained some forms of alkali-soluble silica, no correlation was found between reactive silica content and the expansion in alkali. He believed that the expansion did not seem to be due to the classical alkali-aggregate reaction and expansion might relate with dedolomitization of dolomite attacked by alkali solutions. Gillott [3] suggested that expansion of certain fine-grained argillaceous dolomitic limestones was attributed to an increase in solid volume that resulted from water uptake by clays. He suggested that dedolomitization did not account directly for the expansion as the volume of the solid products was less than the volume of the dolomite reacted. Tang et al. [4] based on results of TEM/EDAX suggested that the expansion was caused by growth and rearrangement of the products of dedolomitization, particularly brucite. Deng et al. [5] and Tong [6] recorded expansion of compacts of dolomite powder-cement and suggested that expansion of alkali-carbonate reaction (ACR) was resulted from pressure of crystallization of calcite and brucite formed in a confined space by dedelomitization.

However, Katayama [7] predicted that ACR was a combined reaction of deleteriously expansive ASR of crypto-crystalline quartz and harmless dedolomitization of dolomitic aggregate. Recently, Katayama et al. [8-10] had some analyses on so-called ACR-affected Canadian filed concretes in Ontario, field concretes from Gananoque, Kingston and Cornwall of Ontario, tested RILEM concrete microbars and tested CSA concrete prisms contained Pisttburg aggregates, and tested RILEM concrete microbars containing an Austria dolostone by means of a combination of polarizing microscopy, SEM observation and quantitative EPMA (EDS) examination. They found that the Pittsburg aggregates contained 3.2wt% or 4.8wt% quartz, most of which was believed to be cryptocrystalline quartz, and that cracks in the specimens were filled or lined with ASR gels. Accordingly, they concluded that ASR gels were the main products responsible for the crack formation in concretes. They also claimed that dedolomitization was harmless because no expansion cracks formed in the cement paste with the Austria dolostone aggregate and that cryptocrystalline quartz might react with brucite from dedolomitization to form Mg-silicate gels because substances composed mainly of Mg and Si were detected by the quantitative analysis of SEM-EDS. After carried out a detailed analysis on the amount, particle size, crystallinity index and dissolved silica in NaOH solutions of quartz in acid-insoluble residue of #78-16 dolomitic limestones from Pittsburg quarry in concrete core of a sidewalk in Kingston, Grattan-Bellew et al. [11] suggested that the Kingston dolomitic limestone with about 10% quartz, at least from the horizon that was tested, exhibited a type of alkali-silica reactivity and therefore concluded that so-called ACR-affected concrete of sidewalk was just deteriorated by ASR.

Experimental results obtained by Katayama et al. [8-10] and Grattan-Bellew et al. [11] seem to indicate that some dolomitic limestones from Pittsburg quarry were alkali-silica reactive. However, their works do not give enough evidence to rule out the effect of ACR on specimens contained dolomitic limestones from Pittsburg quarry. In this paper, expandability of some dolomitic limestones and limestones with different amounts of quartz selected from a few quarries of China were examined according to RILEM AAR-5 concrete microbar test. Content of unreacted quartz in these rocks soaked in NaOH solutions and/or in concrete microbars was determined by a selective solution method with phosphoric acid. Reaction products from ASR and ADR were analyzed by XRD and SEM, and cracking patterns in the tested concrete microbars were investigated by SEM and OM. It is expected to confirm the expandability of ADR in dolomitic limestones in which few of quartz is attacked by alkali solutions.

2 MATERIALS AND METHODS

2.1 Materials

2.1.1 Cement and chemical agents

Portland cement from Jiangnan-Onado Cement Limited Company in Nanjing, China was used. The contents 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 were 20.54%, 4.49%, 3.16%, 65.32%, 0.95%, 0.64%, 0.09%, 2.29% and 2.46%. Alkali content was 0.51% Na_2Oeq. Chemically pure NaOH, phosphoric acid and HCl were used.

2.1.2 Rocks

15 rock samples at Ordovician age from Shandong, Hebei and Hubei provinces of China were used. 8 samples of dolomitic limestones designated as CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 were used to evaluate expandability of ADR. 7 samples of limestones designated as GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06 were used as control samples.

The content of SiO_2 in dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 was 5.98%, 2.20%, 3.21%, 3.81%, 3.16%, 3.24%, 2.93% and 2.90%, respectively. The content of MgO in dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 was 3.99%, 5.90%, 6.00%, 3.10%, 4.24%, 2.34%, 4.38% and 1.69%, respectively. The content of SiO_2 in limestones GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06 was 2.63%, 1.78%, 4.86%, 4.98%, 8.50%, 2.89% and 1.78%, respectively. The content of MgO in limestones GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06 ranged from 0.11% to 0.97%.

Dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 were composed of calcite, dolomite and quartz as shown in Fig. 1. Limestones GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06 were consisted of calcite and quartz.

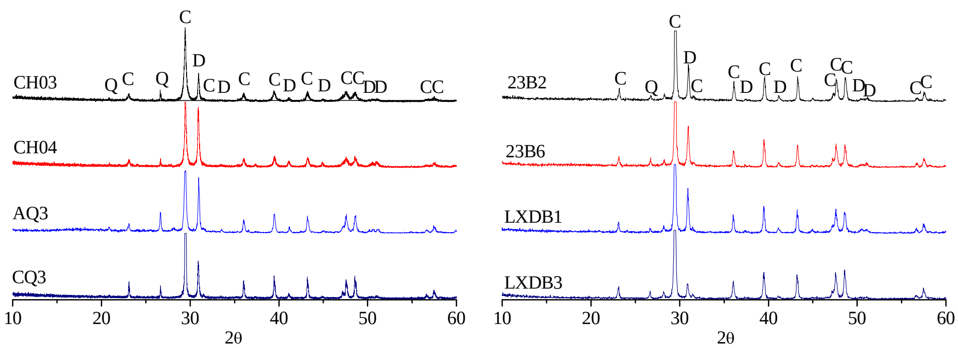


Fig. 1 XRD patterns of powders of rocks CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3

C-Calcite, D-Dolomite, Q-Quartz

Content of quartz in the rock samples was analyzed by a selective dissolution method with phosphoric acid similar to one mentioned by Katayama [7]. Rock powders with particle size less than 0.080mm were placed to 250ml evaporation pan and 1:1 HCl was added to the pan which was then set on 100 ^{o}C water steam. 1:1 HCl was continuously added till no bubble escaped from the solutions. Unreacted rock powders in the pan were dried by 100^{o}C water steam. 25ml 85wt% phosphoric acid was added into dried unreacted rock powders which were heated by 100^{o}C water steam untill the solution in the pan became transparent. The pan was cooled to 20^{o}C and solids in the solution were separated by filtering with quantitative filter papers. The separated solids were repeatedly washed with 60-70^{o}C distilled water, dried at 105 ^{o}C and weighed. The obtained solids were treated as quartz in rocks. The content of quartz in dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 was 5.76%, 1.47%, 3.20%, 2.54%, 2.96%, 3.11%, 2.83% and 2.55%, respectively. It was 2.41%, 1.54%, 4.40%, 4.57%, 7.98%, 2.98% and 3.51% for limestones GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06, respectively.

The dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 were mainly composed of micrite and/or sparite calcite. There were a few of scattered quartz and less than 0.5vol% micro-crystalline quartz. 6vol% to 25vol% of dolomites in 10-80μm were locally and dispersedly distributed in a matrix mainly composed of micrite and/or sparite calcite. Typical microstructures of dolomitic limestones are demonstrated in Fig. 2. Limestones GZK7-2, HZK5-2, SZK1, SZK14-2, YLT, MJG05 and MJG06 were mainly composed of micrite and/or sparite calcite. There were a few of scattered quartz crystals and approximately 0.5vol%, 1vol%, 0.5vol%, 2vol%, 2vol% and 1vol% micro-crystalline quartz in them. There was 10vol% chert nodule composed of 20vol% quartz and

80vol% micro- to crypto-crystalline quartz in limestone YLT. No dolomite was observed in the limestones.

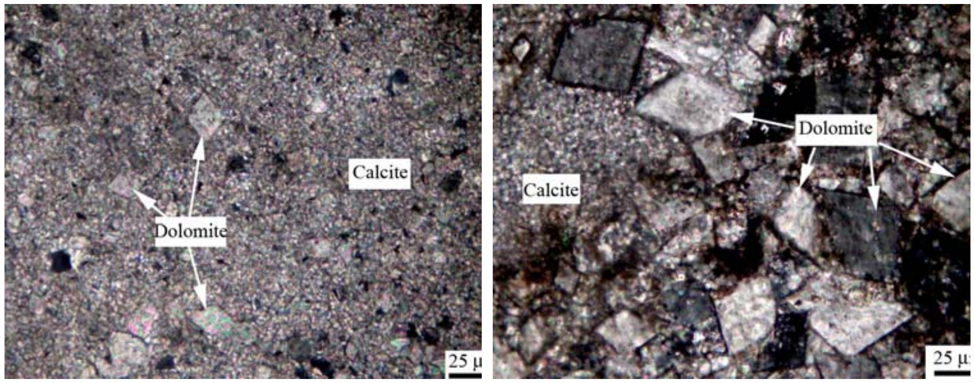


Fig. 2 Typical microstructures of the dolomitic limestones

2.2 Test methods

Concrete microbars were prepared according to RILEM AAR-5 [12]. Alkali 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 for 28 days or 360 days. Length of the microbars was measured by a comparator.

The content of quartz in less than 0.080mm rock powders soaked in 1mol/l NaOH solutions (ratio of rock powders to solutions was 10) at 80^{o}C and 4-8mm crushed rock aggregates derived from the tested concrete microbars was analyzed by a selective solution test with phosphoric acid as described in 2.1.2.

Tested concrete microbars were submitted to petrographic examination to reveal crack patterns. 4-8mm crushed rock aggregates derived from the tested concrete microbars were examined by ARL X'TRA x-ray diffractometer and Hitachi S4800 cold field SEM to detect reaction products.

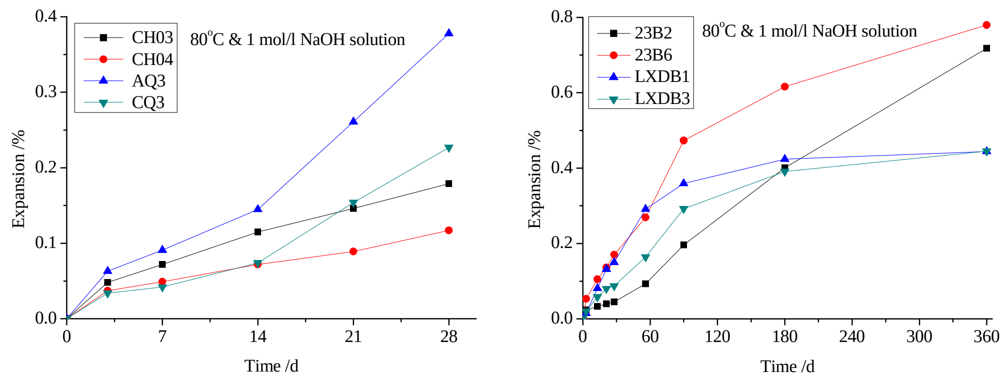
3. RESULTS

3.1 Expansion of concrete microbars

Fig. 3 and Fig. 4 give expansion of RILEM AAR-5 concrete microbars prepared with dolomitic limestones and limestones.

Expansions of concrete microbars with dolomitic limestones CH03, CH04, AQ3 and CQ3 increased with curing age and reached 0.179%, 0.117%, 0.378% and 0.227% at age of 28 days. Expansions of concrete microbars with dolomitic limestones 23B2, 23B6, LXDB1 and LXDB3 were 0.045%, 0.170%, 0.150% and 0.087% at age of 28 days, and 0.718%, 0.780%, 0.444% and 0.445% at age of 360 days. The expansions at 28 days of the microbars contained dolomitic limestones CH03, CH04, AQ3, CQ3, 23B6 and LXDB1 were higher than 0.10%. Although expansions of the microbars with dolomitic limestones

23B2 and LXDB3 were less than 0.10% at age of 28 days, they reached 0.718% and 0.445% at age of 360 days. These results indicate that the dolomitic limestones were expansive in alkali solutions.



(a) Cured for 28 days (b) Cured for 360 days

Fig. 3 Expansions of RILEM AAR-5 concrete microbars with 4-8mm crushed rocks CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3

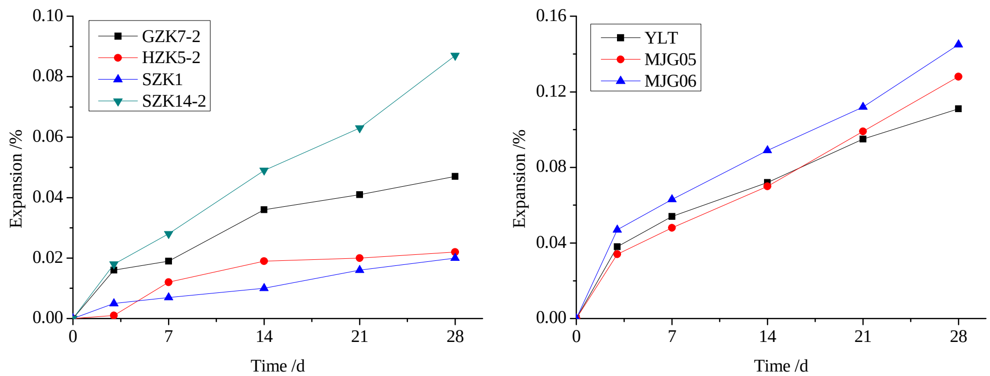
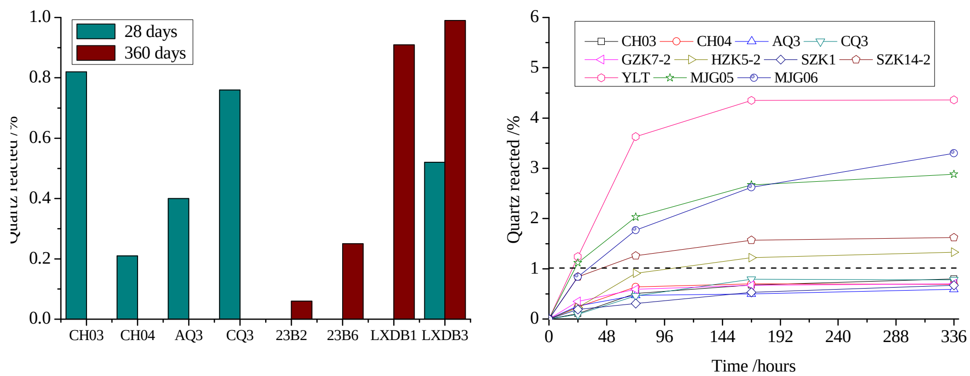


Fig. 4 Expansions of RILEM AAR-5 concrete microbars with 4-8mm crushed rocks GZK7-2, HZK5-1, SZK1, SZK14-2, YLT, MJG05 and MJG06

Expansions of concrete microbars with limestones GZK7-2, HZK5-1, SZK1, SZK14-2, YLT, MJG05 and MJG06 were 0.047%, 0.022%, 0.020%, 0.087%, 0.111%, 0.128% and 0.145% at age of 28 days, respectively. Limestones GZK7-2, HZK5-1, SZK1 and SZK14-2 may be classified as non-expansive because the expansions at 28 days of the microbars were all less than 0.10%. However, limestones YLT, MJG05 and MJG06 with 0.111%, 0.128% and 0.145% expansion at 28 days were expansive.

3.2 Content of quartz in reacted rock samples

The content of quartz in rock samples was analyzed by a selective solution test with phosphoric acid as described in section 2.1.2. Results are shown in Fig. 5. The reacted quartz in 4-8mm aggregates of concrete microbars cured for 28 days was 0.82%, 0.21%, 0.40%, 0.76% and 0.52% for dolomitic limestones CH03, CH04, AQ3, CQ3 and LXDB3. The reacted quartz in 4-8mm aggregates of concrete microbars cured for 360 days was 0.06%, 0.25%, 0.91% and 0.99% for dolomitic limestones 23B2, 23B6, LXDB1 and LXDB3. Quartz reacted in less than 0.080mm powders of the dolomitic limestones was rapidly increased before 72 hours and tended to be in a constant amount at 336 hours. The reacted quartz in powders of dolomitic limestones CH03, CH04, AQ3 and CQ3 at 336 hours was 0.69%, 0.59%, 0.78% and 0.80%. These results are comparable with the content of reacted quartz in 4-8mm aggregates. The reacted quartz in less than 0.080mm powders of limestones GZK7-2, HZK5-2, SZK1, SZK14-2 YLT, MJG05 and MJG06 at 336 hours was 0.67%, 1.26%, 0.67%, 1.62%, 4.36%, 2.88% and 3.30%.



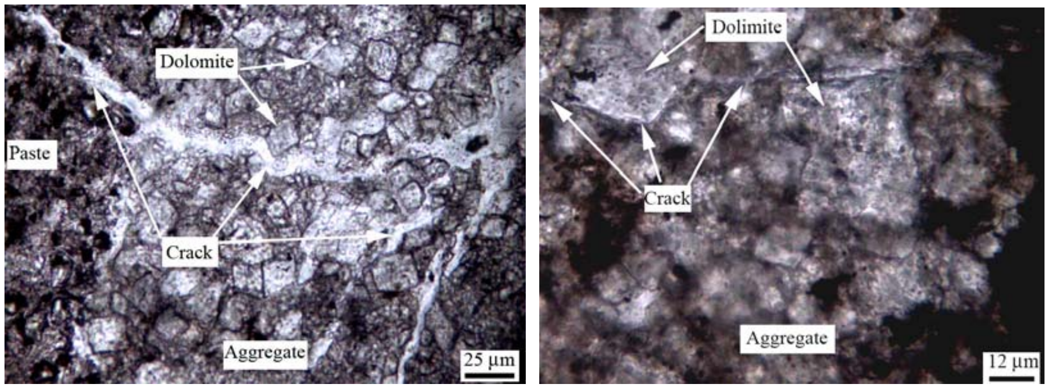
(a) 4-8mm crushed aggregates in the microbars (b) Less than 0.080mm powders in alkali solutions

Fig. 5 Quartz reacted in 4-8mm crushed rocks derived from RILEM AAR-5 microbars and in less than 0.080mm powders soaked in 80^{o}C 1mol/l NaOH solutions (ratio of rock powder to solution was 10)

3.3 Microstructures of concrete microbars

Fig. 6 shows typical crack patterns of the microbars cured for 28 days. Many cracks were originated from dolomite-rich zones in dolomitic limestone aggregates and extended to pastes (Fig. 6(a)). A few of cracks were found to be developed along the interface of dolomite-matrix of calcite (Fig. 6(b)). They were basically empty except that few of cracks were filled with substance like alkali-silica gel. However, most cracks in aggregate of limestone MJG05 were filled with ASR gel.

SEM analysis on aggregates of dolomitic limestones in the concrete microbars revealed that some dolomite crystals were altered to form fine products and a few of cracks were brought about along boundary of dolomite and matrix of calcite as indicated by Fig. 7. Fig. 8 is X-ray diffraction pattern of powdered dolomitic limestone 23B6 derived from concrete microbars cured in 1.0 mol/l NaOH solutions at 80°C for 360 days. Brucite was formed in the dolomitic limestone 23B6.



(a) Crack in aggregate CH03 and paste (b) Crack in aggregate LXDB3

Fig. 6 Crack patterns of dolomitic limestone aggregates CH03 and LXDB3 in concrete microbars cured in 80°C 1mol/l NaOH solutions for 28 days

4. DISCUSSION

4.36%, 2.88% and 3.30% quartz in powders of limestones YLT, MJG05 and MJG06 contained 7.98wt%, 2.98wt% and 3.51% quartz were reacted by 1 mol/l NaOH solutions at 80°C, as shown in Fig. 5. ASR from these reacted quartz caused 0.111%-0.145% expansion in RILEM AAR-5 concrete microbars cured for 28 days, respectively. 0.70%, 1.26%, 0.67% and 1.62% quartz in powders of limestones GZK7-2, HZK5-1, SZK1 and SZK14-2 contained 2.41wt%, 1.54%, 4.40wt% and 4.57% quartz were reacted by 1 mol/l NaOH solutions at 80°C. ASR from these reacted quartz brought 0.047%, 0.022%, 0.020% and 0.087% expansion in RILEM AAR-5 concrete microbars cured for 28 days, respectively. Expansions of the specimens contained with limestones GZK7-2, HZK5-1, SZK1 and SZK14-2 and tested according to NF P188-588, ASTM C1260 and ASTM C1293 were less than 0.057% at 6h, 0.092% at 14 days and 0.026% at 1 year, respectively. They were all classified as non-reactive. The content of quartz that may be reacted with alkali solutions is perhaps a key parameter to determine alkali-silica reactivity of limestones. Limestones with more than 2.0% reacted quartz as measured in this investigation might bring about greater than 0.10% expansion in RIELM AAR-5 concrete microbars at 28 days. Limestones with lower than 1.5% reacted quartz may not produce greater than 0.10% expansion in the microbars.

Dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 contained 5.76%, 1.47%, 3.20%, 2.54%, 2.96%, 3.11%, 2.83% and 2.55% quartz, respectively. The content of reacted quartz in them ranged from 0.06% to 0.99% during the test period.

If 1.0% reacted quartz is set as threshold value for 0.10% expansion of RILEM AAR-5 concrete microbars due to ASR based on above analysis on limestones GZK7-2, HZK5-1, SZK1, SZK14-2, YLT, MJG05 and MJG06, it may be deduced that 0.179%, 0.117%, 0.378%, 0.227%, 0.170% and 0.150% expansion of the concrete microbars with dolomitic limestones CH03, CH04, AQ3, CQ3, 23B6 and LXDB1 at age of 28 days and 0.718%, 0.780%, 0.444% and 0.445% of expansion with 23B2, 26B6, LXDB1 and LXDB3 at age of 360 days cannot be completely attributed to ASR of the reacted quartz. ADR as revealed by SEM and XRD in Fig. 7 and Fig. 8 might take a significantly contributing role in expansion of the concrete microbars. Empty cracks originated from reacted dolomite-rich zone in dolomitic limestone aggregates to surrounded cement pastes as demonstrated by Fig. 6 may be an evidence to support above conclusion on expandability of ADR.

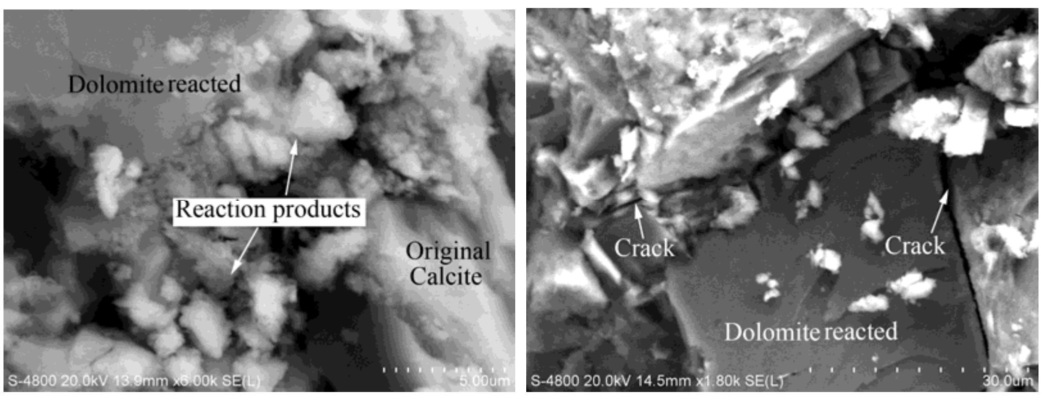


Fig. 7 Reacted dolomite, reaction products and cracks induced in dolomitic limestone aggregates of concrete microbars cured in 1.0 mol/l NaOH solutions at 80°C for 28 days

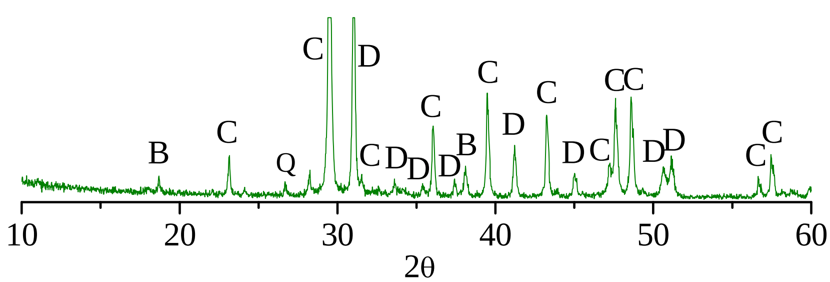


Fig. 8 XRD pattern of powdered dolomitic limestone 23B6 derived from concrete microbars cured in 1.0 mol/l NaOH solutions at 80°C for 360 days

C-Calcite, D-Dolomite, Q-Quartz, B-Brucite

5. CONCLUSIONS

(1) Alkali-dolomite reaction of dolomitic limestones CH03, CH04, AQ3, CQ3, 23B2, 23B6, LXDB1 and LXDB3 with less than 1.0% reacted quartz in RILEM AAR-5 concrete microbars might play a significantly contributing role in expansion of the concrete microbars. In other words, ADR might bring about expansion in the concrete microbars.

(2) 4.36%, 2.88% and 3.30% reacted quartz in limestones YLT, MJG05 and MJG06 might cause RILEM AAR-5 concrete microbars to expand larger than 0.10% at 28 days. While 0.70%, 1.26%, 0.67% and 1.62% reacted quartz in limestones GZK7-2, HZK5-1, SZK1 and SZK14-2 did not bring about larger than 0.10% expansion in RILEM AAR-5 concrete microbars at 28 days.

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