CONCURRENCE OF ALKALI-SILICA AND ALKALI-DOLOMITE REACTION

Tong Liang* and Tang Mingshu**

*Department of Civil Engineering
Tsinghua University, Beijing 100084
**Department of Materials Science and Engineering
Nanjing University of Chemical Technology
Nanjing, 210009, P. R. of China

ABSTRACT

For several Chinese aggregates, it is found that both fine grain dolomite and reactive microcrystalline quartz or chalcedony presented in a single aggregate particle. After studying by autoclave micro-mortar and concrete bar, it is observed that when fine grain dolomite and poor crystallized quartz mix and evenly distribute in the rock, both mortar and concrete will show considerable expansion. However, when dolomite and quartz or chalcedony distributed separately, only mortar bars can present high expansion. It is most likely that both alkali-silica and alkali-dolomite reactions may be involved in the former aggregate. SEM-EDAX and XRD results confirmed this suggestion. For the latter case, however, almost no reaction product was detected between dolomite grains though visible silica gel fills the cracks of the concrete bar. Considering the above results, the authors further suggested that for a given aggregate there exist a certain degree of combination of pure ASR and ACR.

Keywords: Alkali-carbonate reaction, Alkali-silica reaction, Expansion mechanism, Microstructure.

INTRODUCTION

Alkali-aggregate reaction is usually divided into two categories: alkali-silica and alkali-carbonate reaction (Tang 1992). Researchers usually deal with these two deleterious processes separately. However, reactive silica may commonly present in some siliceous carbonate aggregates especially for some fine-grained dolomitic limestones or dolomites (Regourd 1989, Fournier et al. 1989, 1990, French 1992). Then, both ASR and ACR should be considered. Dr. Idorn reminded that some published cases of deleterious ACR may actually have been cases of deleterious ASR (Idorn 1992). However, there is another argument that ACR may be of significant effects on some known ASR deterioration. This paper purports to present some facts that both ASR and ACR occur in one aggregate.

MATERIALS AND EXPERIMENTAL METHODS

Several siliceous dolomites and a dolomite-bearing chert were available. Except quartzite (Q), a control sample, all these rocks contained fine-grained dolomite crystals and poorly crystallized microcrystalline quartz or chalcedony and very little amount of calcite and clays. The chemical compositions of these rocks are listed in Table 1.

The alkali reactivity of the rocks was evaluated by autoclave mortar bar (Tang et al. 1983) and concrete microbar as well as rock prism (Tang et al. 1994) method. Several concrete microbars and rock prisms were polished to expose the aggregate particles. The surface appearances of the bars were observed under an optical microscope to distinguish cracks' formation and growth after curing for periods of times. The parts of interest may be further investigated by SEM-EDXA.

Table 1 Chemical compositions of the tested rocks and the cement used

	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3
NM-2	21.72	24.29	15.70	1.23	0.56
NK-D	8.51	27.68	19.03	0.25	0.84
NK-DQ	47.43	14.54	9.64	0.22	0.73
NK-Q	82.45	4.87	3.4	0.15	0.53
HL	16.82	25.52	17.99	0.30	0.27
Q	98.82	0.53	0.34	0.16	0.09
Portland Cement	20.72	61.39	1.23	4.91	4.23

RESULTS AND DISCUSSIONS

Petrographic Texture of the Rocks

Dolomite NM-2 composed of fine-grained dolomite (2-4 μm in size) and crypto-crystalline quartz scattered evenly in dolomite mosaic. A little amount of calcite and clay minerals presented in the rock as well. XRD analysis showed the quartz was in poor crystallization (Tong et al. 1995). The specimen NK-D, NK-DQ and NK-Q were of the same origin and similar petrographic texture. They consisted of fine-grained dolomite and high-strained quartz. Dolomite and quartz were found in veins as shown in Figure 1 for NK-DQ and NK-Q. Quartz in NK-D scatted evenly in dolomite mosaic. The main difference among the three was silica content. The largest amount of quartz presented in NK-Q. Petrographic characteristics and composition of dolomite HL was similar to those of NK-DQ, although it has a different origin. The coarse-grained quartzite sample (Q) was composed of pure and well-crystallized quartz.

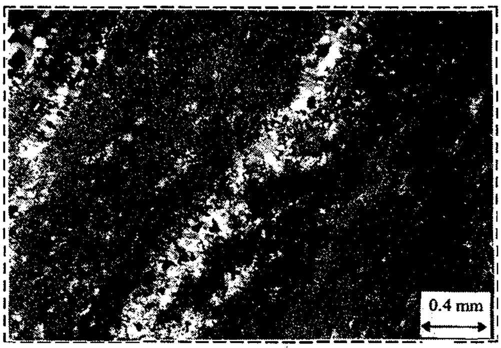


Figure 1 Petrographic texture of NK-DQ rock sample showing fine-grained dolomite and microcrystalline quartz

Expansive Behaviors

The autoclave mortar bar test showed that all the tested samples were reactive except for the quartzite (Table 2). These results agreed with the findings of the previous petrographic examinations. Considering the possible alkali-carbonate reactivity, the rocks were tested using newly developed autoclave microbar method. The results are shown in Figure 2.

It was noted that the expansion was sensitive to the petrographic characteristics. When microcrystalline quartz was evenly scattered in the intergrains of dolomite mosaic like the case of NM-2 and NK-D, the expansion was great. For NK-D, silica contained was less than that in NM-2 and some of them were in well crystallization, and thus lower expansion was observed. Slight expansion is for the sample NK-DQ and NK-Q in which the amount of dolomite and silica distributed in streaks in veins individually. The well-crystallized quartzite (Q) presented only negligible length changes.

Table 2 The test results of autoclave mortar bar method

Aggregate/Cement	NM-2	NK-D	NK-DQ	NK-Q	HL	Q
1:10	0.163	0.68	0.102	0.143	0.901	0.018
1:5	0.211	0.92	0.135	0.165	0.122	0.018
1:2	0.220	0.113	0.154	0.166	0.131	0.025

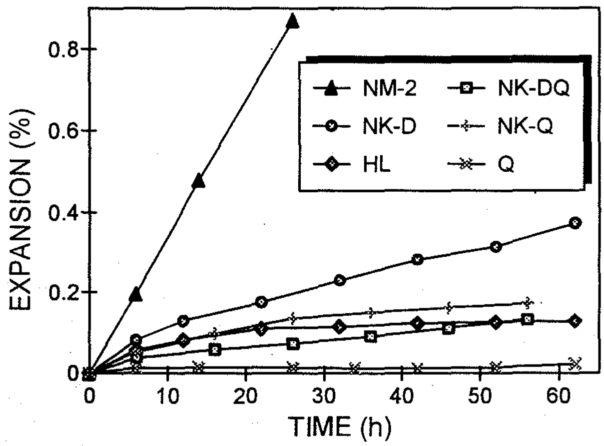


Figure 2 Concrete microbar expansion of the selected rocks

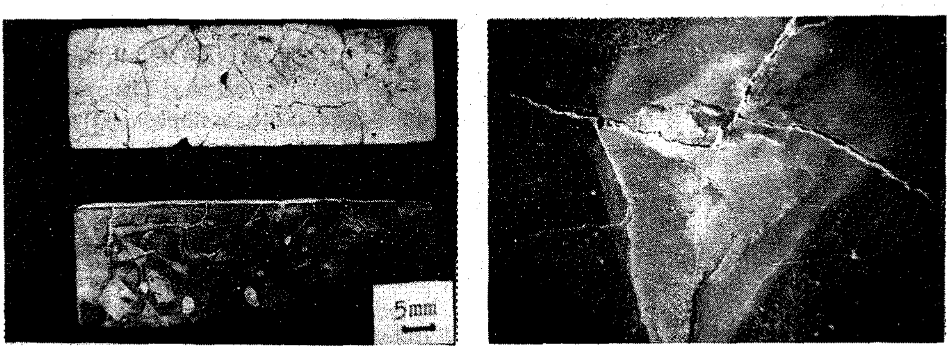


Figure 3 Cracks (overall and zoomed) on the surface of NM-2 concrete microbars after autoclaving at 150℃ in 10% KOH solution for 22 hours

As shown in Figure 3, considerable crack was observed on the surface of NM-2 concrete bars, and no visible silica gel was observed in the cracks. However, for NK-Q and NK-DQ, all cracks filled with transparent gel after 30 hours autoclaving. Although considerable expansions were also found for NM-2 rock prisms (Figure 4), no cracks presented on the rock surface. When cured at 60°C in 10% KOH solution, concrete microbars containing NM-2 also showed rapid expansion as shown in Figure 5.

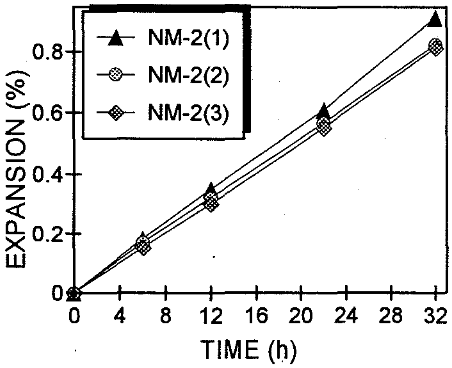


Figure 4 Expansion of rock prisms autoclaved at 150℃ in 10 % KOH solution.

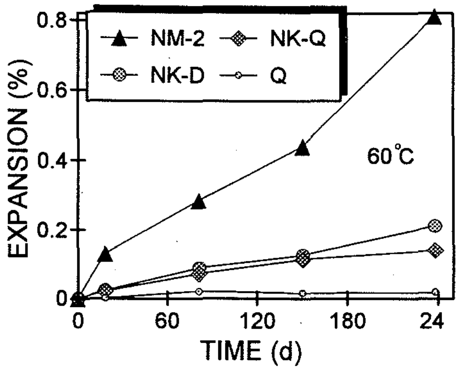
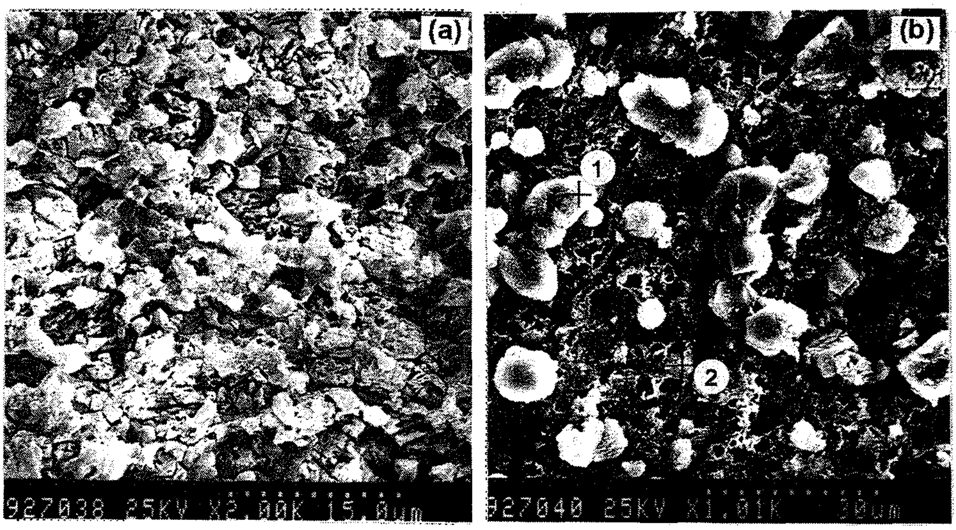


Figure 5 Expansion of concrete microbars cured at 60℃ in 10 % KOH solution

Microstructural Investigations

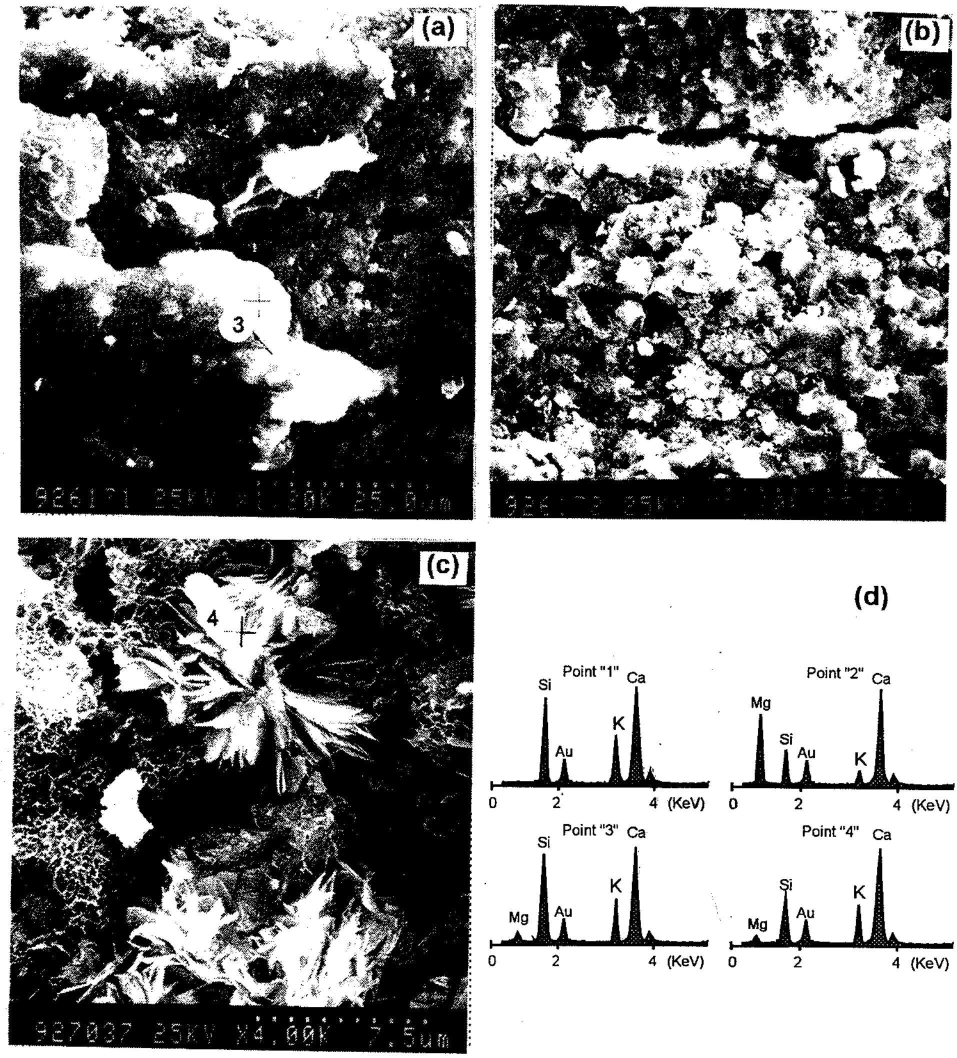
In order to reveal the expansion mechanism, investigations were performed on the microstructural changes due to the reactions occurred. First, it was studied the changes on the polished NM-2 slice surface before and after autoclaving in 10 % KOH solution. Both dedolomitization and silica gel formation were observed. XRD data showed the presence of calcite and brucite, and no other products produced although the intensity the silica lines reduced considerably. Compared with dedolomitization occurred on the pure dolomite surface (Tong 1994), it was noted that certain amount of silica introduced in the reaction, and changed a little bit of the morphology of brucite



(a) Original polished surface etched by dilute HCl solution.
(b) Reacted surface showing silica gel around calcite (floating grains) and the brucite layer incorporating some silica.

Figure 6 SEM morphology of the dolomite NM-2 surface before and after autoclaving at 150℃ in 10 % KOH solution.

as shown in Figure 6. EDXA results presented silica containing in the brucite layer (Figure 7). Considering the findings on the possible reaction between dolomite and opal in KOH solution (Tong 1994), it seemed that gel like a product so-called C-M-S-H may produce in this layer. Although determining the exact process was hard, it was most likely that the C-M-S-H product was produced by the reaction between silica and brucite.



(a) Alkali-silica gel in the outermost later of the reaction rim.
(b) Inner layer of the reaction rim showing the main (parallel to the surface) and the minor crack.
(c) Spongy and rosette-like gels deposit in the main cracks.
(d) EDXA results of the marking points

Figure 7 SEM morphology of the reaction rim of NM-2 rock prism autoclaved at 150℃ in 10 % KOH solution for 30 hours.

As mentioned early, although considerable expansion for NM-2 rock prisms had been observed, no visible cracks were found on the rock surface. However, after the prism broken, cracks or cracking planes parallel to the prism surface can be easily distinguished inside the reaction rim. The total width of the rim was about 1 mm after autoclaving for 30 hours and was separated into four or three layers by the cracks. The morphologies of the reaction rim, products deposited in cracks and the EDXA results of the marking points are shown in Figure 7. It was found that alkali-silica gel formed in the reaction rim and the cracks. Intensive reaction was found in the outermost layer. Similar to the case found in other reactive carbonate rocks, it was also noted that obvious signs of reactions were shown at the center of the prism (away from the rims) as in Figure 8. XRD studies showed that both silica and dolomite involved in the reaction, however, no brucite was found including in the reaction rims and the inside region.

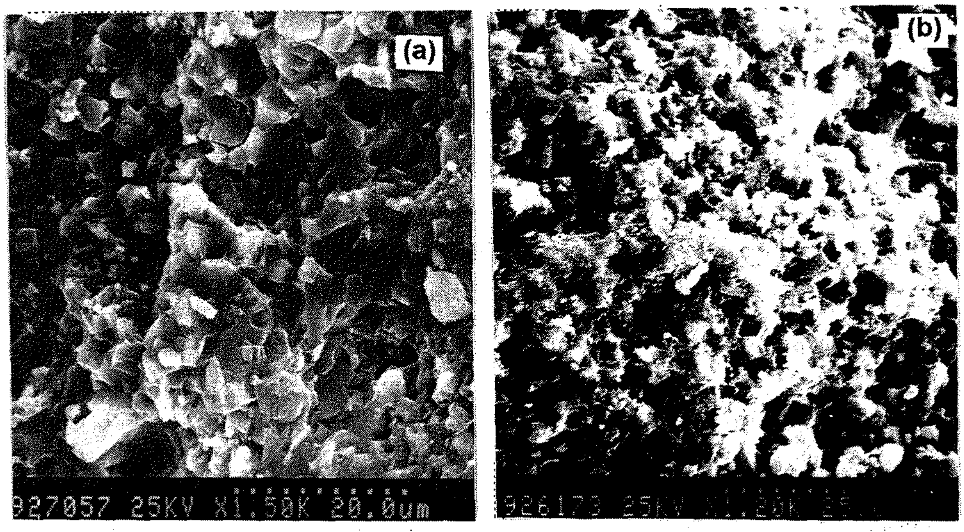


Figure 8 The central part of the MN-2 prism (a) before and (b) after autoclaving at 150℃ in 10 % KOH solution

Because dolomite and quartz containing in NK-DQ, NK-Q and HL were distributed separately, reactions in the particles were almost the same as dolomite and chert respectively. Except for the interfacial reaction, no visible sign of reaction was observed in the dolomite zones like the case of a pure non-reactive dolomite rock, while in silica area it was noted considerable etching of microcrystalline quartz and gel formation at the aggregate-cement interface and extruding into the cracks.

Mechanism of the Expansion

If cryptocrystalline quartz mainly gathered between the inter-grains of dolomite mosaic, when alkali solution penetrated into the aggregate may first dissolve the quartz and reacted with dolomite, and thus gel formation and dedolomitization occurs. Obviously, the presence of quartz is significant in this case. In one aspect, it causes alkali solution penetration more easily; In another aspect, the reaction itself, if the content is enough, may cause expansion.

Therefore, the expansion of concrete microbars and rock prism of NM-2 was the result of the expansive reaction occurred in the aggregate including the reaction rims. In term of chemical reaction, it is hard to separate alkali-silica and dolomite reaction and discusses the weight on the expansion processes. According to the other experimental observations, it is believed that both ASR and ACR occurred in the aggregate and led to the expansion. The expansion of NK-D concrete bars was similar to NM-2. Because far less amount of microcrystalline quartz mixed with dolomite mosaic that reduced the mutually interaction of ASR and ACR and caused the less expansion. As for NK-DQ, NK-Q and HL, the expansion was mainly the result of ASR, because the pure dolomite region prevented from alkali solution penetrated into, and no expansive ACR detected.

Discussions

In other phases of research, the authors found certain amount of silica contained in the reaction products layer at the interface of rhombic dolomite and the surrounding matrix in reactive carbonate rocks though only 5-7% of well-crystallized microcrystalline quartz presented in the rock (Tong 1994). Therefore, generally, if an aggregate contains both fine-grained dolomite and silica, there may be two cases: (1) the two parts as a whole located separately in the aggregates, and (2) the two minerals mixed with each other. The first case can be handled by ASR and ACR as usual. The other case is complicated and can be described in Figure 9.

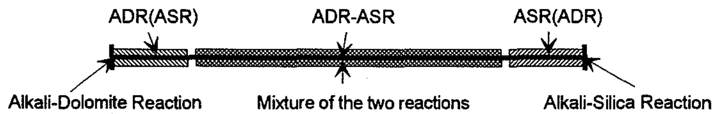


Figure 9 An illustration of the proportion of ADR and ACR in a certain aggregate particle

The two extreme cases, alkali-dolomite reaction and alkali-silica reaction, can be plotted at both ends of a line as in the figure. The usually described ACR (or ASR) can sometimes involve a little proportion of ASR (or ACR) for both silica and dolomite containing in an aggregate and can be handled as ACR or ASR alone. However, when ADR and ASR are highly mixed as the case of the rock (NM-2), it is hard to classify the reactions involved. Both dolomite and silica reacted with alkali solution simultaneously and the products formed is a gel-like substance consisting Si, Mg, K, H and O elements as well as a certain amount of calcite. If this case is not rare in concrete, the possibility high expansion should be noted. Now, the exact reaction processes are not clearly understood. It seems that the reaction products and possible expansive forces may be different from ACR and ASR. It may be valuable to learn whether the existence of ASR (or ACR) may enhance ACR (or ASR) or not.

It is well known that mortar-bar methods are the effective methods to detect ASR while concrete methods can evaluate both ASR and ACR of all rock types. Alkali-carbonate reactive rocks usually do not present excessive expansion when tested by mortar-bar methods. However, it indeed expressed a certain amount of expansion. When in the presence of little reactive silica, the expansion may exceed the criteria of distinguishing reactive and non-reactive aggregates. In other words, the alkali-silica reactive aggregates detected by mortar bar method do not necessarily mean that ASR is the only possible reaction occurred in the bars if the rock involves fine grained dolomite. Therefore, petrographic and microstructural investigation are very significant to justify the expansion causes.

CONCLUSIONS

If an aggregate contains both fine-grained dolomite and reactive silica, when the two parts distributed separately such as in veins or streaks, the expansion of concrete can be handled by ASR or ACR alone, and when the two reactive minerals mix with each other, it is most likely that both ASR and ACR may occur. If ASR and ACR occur in an aggregate, it is hard to distinguish the roles on the expansion using the expansion test methods. Thus, petrographic and microstructure investigation are necessary.

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