Pergamon

Cement and Concrete Research 32 (2002) 763–768

CEMENT AND CONCRETE RESEARCH

Expansion of siliceous and dolomitic aggregates in lithium hydroxide solution

Guangren Qian[a,*], Min Deng[b], Minshu Tang[b]

[a]Southwest University of Science and Technology, Mianyang 621002, Sichuan, China
[b]Nanjing University of Technology, Nanjing 210009, Jiangsu, China

Received 2 June 2000; accepted 7 December 2001

Abstract

Autoclave expansion behaviors of siliceous and dolomite-bearing aggregates in LiOH and KOH solutions were studied. The results show that lithium hydroxide can suppress ASR expansion and induce ACR expansion. It is the duplex effect of lithium hydroxide that could be used for exploring the mechanism responsible for the expansion of dolomite-bearing aggregates in alkali environments. It has been shown that the expansion of argillaceous dolomite limestone with typical texture from Kingston, Ontario, Canada, can be attributed to ACR rather than to ASR. However, some other argillaceous dolomite limestones exhibit both ACR and ASR. Meanwhile, XRD detected that solid products of dedolomitization in LiOH solution were brucite, calcium carbonate and lithium carbonate with a consequent solid volume increase. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali–carbonate reaction; Lithium hydroxide; Expansion mechanism

1. Introduction

Alkali–carbonate reaction (ACR) is an important type of alkali aggregate reaction (AAR). Excess expansion and cracking of concrete has occurred when some dolomite-bearing aggregates with typical texture have been used as coarse aggregates in concrete with high alkali cement. It is generally agreed that the dedolomitization process, in which dolomite in aggregates is reacted with strong alkali to produce brucite, calcium carbonate and soluble alkali carbonate, is basic and necessary to ACR expansion, regardless of the mechanism responsible for expansion [1–5]. However, the existence of ACR was still doubted by some researchers [6–8] because there exists about 10% or more insoluble residue in the argillaceous dolomitic limestones with higher ACR expansibility [9,10]. Meanwhile, dolomite-bearing aggregates containing microcrystalline or cryptocrystalline quartz are relatively common [11–13]. Therefore, it is difficult to distinguish the contribution of ACR from that of alkali–silica reaction (ASR). Katayama [7] considered that ACR was always associated with ASR; classic ACR that occurs in the argillaceous dolomitic limestone from Kingston, Canada, should be reviewed in terms of ASR of cryptocrystalline quartz hidden in the argillaceous matrix of the aggregates. Thus, it is necessary to develop a way to discriminate ACR from ASR when ACR may coexist with ASR.

Various lithium compounds have been investigated over many years for their effectiveness in mitigating alkali–silica reactivity. Results by McCoy and Caldwell [14], Lawrence and Vivian [15], Sakaguchi et al. [16], Stark [17] and Diamond and Ong [18] verified that lithium compounds were very effective in suppressing ASR. For this reason, lithium hydroxide and other lithium salts have been used as effective additives that reduce the expansion caused by ASR. Compared to suppressing ASR, however, some lithium compounds, such as LiCl, $LiNO_3$ and LiOH, have been shown to be less effective in suppressing ACR expansion [19]. Wang and Gillott [20] detected existence of dedolomitization reactions in lithium hydroxide environment. This suggests that lithium hydroxide seems to have a duplex role in suppressing ASR and inducing ACR. The object of this paper is to present our results about how to verify ACR existence when ACR possibly coexists with ASR by util-

---

* Corresponding author. Current address: EERC, B4b-07, School of Civil and Structural Engineering, Nanyang Technological University, Singapore 639798, Singapore. Tel.: +86-8615-254; +86-7905-077.

E-mail address: cgrqian@ntu.edu.sg (G. Qian).

PII: S0008-8846(01)00757-8

izing opposite controlling effects of lithium hydroxide on ASR and ACR.

2. Experiments

2.1. Aggregates

Four kinds of aggregates were used. Table 1 describes the mineral constitutes of these aggregates. Zeolitized pearlite aggregate RF was taken from Shandong Province, China, and was used as a reactive aggregate with higher ASR expansion. It consists mainly of pearlite-like glass matrix and some chalcedony. Argillaceous dolomitic limestone CK from Kingston, Ontario, Canada, was selected as a reactive aggregate with ACR expansion. The aggregate JH1 from Tianjin, China, was an argillaceous dolomite, in which more than 10% microcrystalline quartz was scattered in dolomite. The dolomite aggregate TL2-3, collected from Sichuan province, China, contains more than 95% dolomite crystal, showing a mosaic texture. It contains only 0.46% acid-insoluble residue.

2.2. Test methods for evaluating alkali reactivity of aggregates

The mortar microbar test method NF P18-588-91 [21] was applied to evaluate alkali–silica reactivity of aggregates. Alkali–carbonate reactivity of aggregates was determined by concrete microbars or rock prisms [22,23]. The criterion used for judging the alkali activity of aggregates is 0.1% of expansion when autoclaved for 6 h at 150 °C.

2.2.1. Concrete microbar test method [22]

After adjusting the cement alkali content to 1.5% Na_2O equivalent by adding KOH into the mixing water, concrete microbars 20×20×60 mm in size were cast with 5–10-mm aggregate at a cement/aggregate ratio of 1.0 and a W/C ratio of 0.3. The bars were removed from the molds after 1-day curing in moist chamber and their original lengths were measured. The concrete microbars were then steamed at 100 °C for 4 h and autoclaved at 150 °C for different periods of time in 10% KOH solutions. The length was measured after the bars had cooled to room temperature. The linear expansions of specimens were calculated. In the tests for evaluating the role of LiOH in AAR, $LiOH{\cdot}H_2O$ compound was used to adjust the cement alkali content to 1.5% Na_2O equivalent and to make up 10% LiOH solutions for autoclave test.

2.2.2. Mortar microbar test method

Mortar microbar test method was followed NF P18-588-1991 [21], except that the ratio of cement to aggregate was 2:1. Ten-percent KOH solutions were used for autoclaving.

2.2.3. Rock prism method

Rock samples were cut into the shape of prism about 10×10×40 mm in size. Pins were cemented on both ends of prisms using Portland cement pastes. After immersion in water for several days to get a constant length, the prisms were autoclaved at 150 °C in alkali solutions (LiOH or KOH) or in water for different periods of time.

3. Results and discussion

To determine potential AAR expansion of various aggregates, mortar microbar test for aggregates was usually the first step. Concrete microbar test was followed and, if necessary, rock prism test was carried out subsequently. Meanwhile, based on many research results indicating that lithium hydroxide and other lithium salts could effectively inhibit ASR and expansion, LiOH solution was employed as a reaction medium of the autoclave test to explore expansive behavior of dolomite-bearing aggregates in LiOH solution.

3.1. Expansion of specimens with siliceous and dolomite-bearing aggregates

3.1.1. Zeolitized pearlite RF

The autoclave expansion of mortar microbars caused by zeolitized pearlite RF is 0.27% at 6 h, being much higher than the criterion of 0.1%. Therefore, the zeolitized pearlite was considered to be alkali–silica reactive. The alkali–silica reactivity of aggregate RF also resulted in a high expansion of concrete microbars in 10% KOH solution, as shown in Fig. 1. The expansion of concrete microbars containing this aggregate exceeded 0.60% at 6 h. This also confirms that the aggregate RF has highly reactive silica components. However, we noticed that if the concrete

Table 1
Lithology and the main minerals of aggregates

Sample	Lithology	Sources	Minerals
RF	Zeolitized pearlite	Shandong, China	> 70% glass matrix, 15% cryptocrystalline zeolite, 2–4% chalcedony and 10% quartz
CK	Argillaceous dolomitic limestone	Kingston, Canada	40–50% dolomite, 40–50% calcite and 11.3 % acid insoluble residue made of illite, quartz and chlorite
JH1	Argillaceous silt Dolomite	Tianjing, China	70–75% dolomite, <5% calcite and 22.3% acid insoluble residue made of microcrystalline quartz and illite
TL2-3	Dolomite with medium crystal size	Sichuan, China	> 95% dolomite, <3% calcite and 0.46% acid insoluble residue

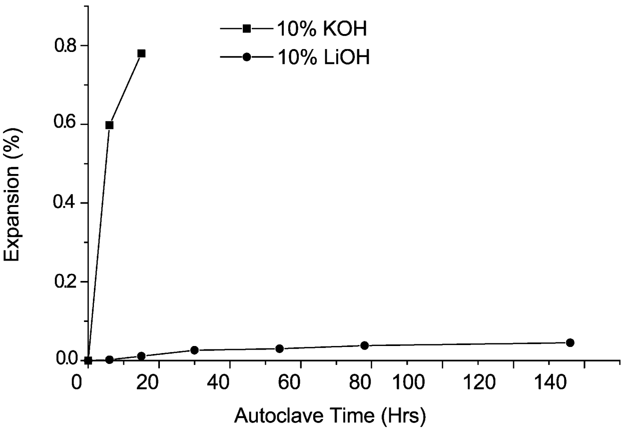


Fig. 1. Autoclave expansion of concrete microbars containing zeolitized pearlite cured at 150 °C.

microbars containing this aggregate were autoclaved in 10% LiOH solution, the expansion at 6 h dropped dramatically and became negligible (Fig. 1). The expansion was still less than 0.04% even if the autoclave time was prolonged to 78 h.

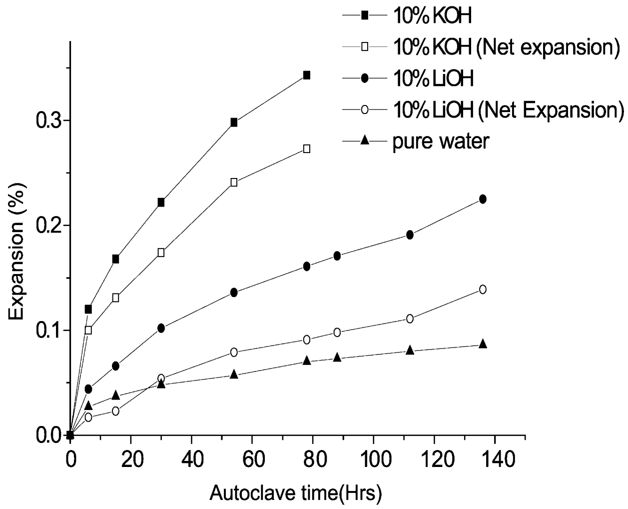
3.1.2. Argillaceous dolomitic limestone CK

The expansion behaviors of the argillaceous dolomitic limestone CK with typical texture from Kingston, Ontario, Canada, have been investigated for several decades. A number of results have proved this aggregate to be alkali–carbonate reactive [1,2,4,10]. Autoclave expansion of mortar microbars containing aggregate CK was only 0.01% at 6 h. This indicates that argillaceous dolomitic limestone CK is not alkali–silica reactive.

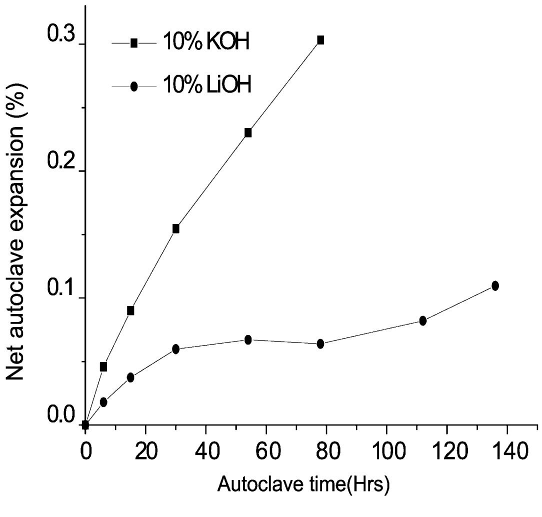
It is generally considered that autoclave expansion of concrete microbars and rock prisms in alkali solutions at 150 °C may be caused by the contributions of several factors, such as expansion either from ACR or from ASR, swelling of clays in the aggregates by absorbing water and heat-induced expansion of aggregate at a high temperature. To evaluate the swelling expansion of clays and the heat-induced expansion of aggregates, concrete microbars or rock prisms were also autoclaved in pure water at 150 °C. From Fig. 2a, 0.09% of expansion was reached when the concrete microbars were autoclaved in pure water for 136 h. This notable expansion should be related to swelling due to water absorption of clay and/or some irreversible heat-induced expansion of aggregate. For this reason, a concept of net AAR expansion was introduced to describe the expansion only resulting from AAR. The net AAR expansion was obtained by subtracting the expansion of specimens autoclaved in pure water from the expansion of specimens treated in alkali solutions.

Fig. 2a also demonstrates the net AAR expansion of concrete microbars containing the aggregate CK. The net AAR expansion of concrete microbar in KOH solutions at 6 h was 0.1%, just getting to the criterion of 0.1%. It is reasonable to consider that this net AAR expansion of concrete microbars containing aggregate CK was due to ACR because the ASR expansion is negligible. When the specimens were continuously autoclaved for up to 78 h in 10% KOH solutions, a net AAR expansion of 0.27% was reached.

To verify whether the net AAR expansion of concrete microbars containing the aggregate CK in KOH solutions is from ACR, the specimens were also soaked in 10% LiOH solutions. Although the net AAR expansion of concrete microbars containing aggregate CK cured in 10% LiOH solutions is only 0.02% at 6 h, being less than that in 10% KOH solutions, it did increase with time. A higher net AAR expansion of 0.14% was given when the specimens were autoclaved for 136 h (Fig. 2a). Thereby, it may be reas-



(a) Concrete microbars



(b) Rock prisms

Fig. 2. Autoclave expansion of argillaceous dolomitic limestone CK in alkali solutions (150 °C).

onably concluded that this net AAR expansion should be only attributed to the lithium–dolomite reaction because reactive silica, such as microcrystalline quartz and siliceous glass, did not produce any significant ASR expansion in LiOH solutions as shown in Fig. 1.

Rock prism tests of the aggregate CK were also carried out. Fig. 2b gives the results. The net AAR expansions of rock prisms CK in 10% KOH solutions were higher than in 10% LiOH solutions. Similarly, the net AAR expansion of rock prisms CK soaked in LiOH solutions was as high as 0.11% when autoclaved for 136 h. This further confirms that the argillaceous dolomitic limestone CK has caused ACR expansion.

3.1.3. Dolomite TL2-3

There exists very little clay and silica in dolomite TL2-3. The aim of selecting such a nearly pure dolomite for testing is to avoid the potential interference from reactive silica, clay and other substances with the ACR mechanism. Fig. 3a illustrates the net AAR expansion of concrete microbars containing this dolomite in different solutions. When autoclaved in 10% KOH solutions for 6 h, the net AAR expansion of specimens was only 0.03%, much less than the criterion 0.1%. Thereby, this dolomite should be reckoned as not alkali–carbonate reactive. However, the net AAR expansion was increased continuously with time, being as high as 0.18% at 136 h.

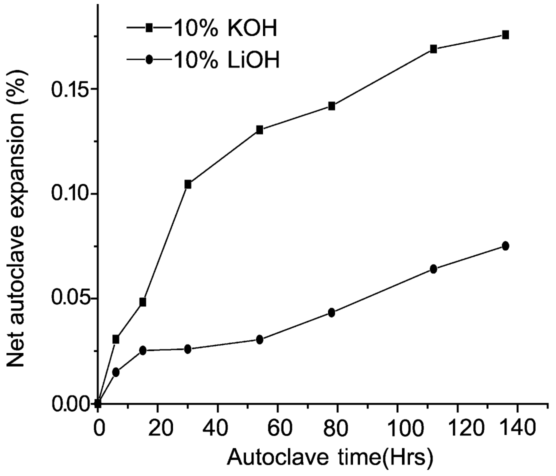
When the concrete microbars with dolomite TL2-3 were autoclaved in 10% LiOH solutions, they produced much less expansion than in KOH solutions, as shown in Fig. 3a. However, the net AAR expansion of specimens also increased with time. The expansion of 0.08% could be observed at 136 h.

The net AAR expansion of rock prisms TL2-3 cured in LiOH solutions became more considerable, as demonstrated in Fig. 3b. It approached 0.08% at 15 h and 0.17% at 136 h. Additionally, rock TL2-3 caused a larger expansion in LiOH solutions than in KOH solutions when autoclaved for the same time. This behavior is quite different from that for the argillaceous dolomitic limestone CK.

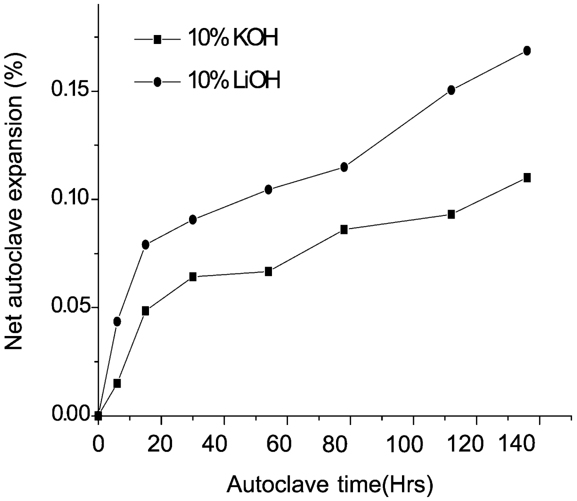
3.1.4. Argillaceous silt dolomite JH1

The autoclave expansion of mortar microbars containing argillaceous silt dolomite JH1 at 6 h was 0.14%. This indicates that the aggregate JH1 to be highly alkali–silica reactive. The reactivity of this rock was brought about by more than 10% microcrystalline quartz scattered in dolomite crystals with a mosaic texture.

Fig. 4a illustrates the net AAR expansions of concrete microbars autoclaved in 10% KOH solutions and in 10% LiOH solutions. They developed slowly during the first 15 h and then increased rapidly with autoclave time when cured in 10% KOH solutions. The net AAR expansion of the concrete microbars in 10% LiOH solutions developed steadily during the whole period and reached 0.15% at 136 h. This expansion in LiOH solutions should be attributed to ACR. The expansion of concrete microbars in 10% KOH solutions may be brought about by both ACR and ASR.



(a) Concrete microbars



(b) Rock prisms

Fig. 3. Net AAR expansion of dolomite aggregate TL2-3 in alkali solutions (150 °C).

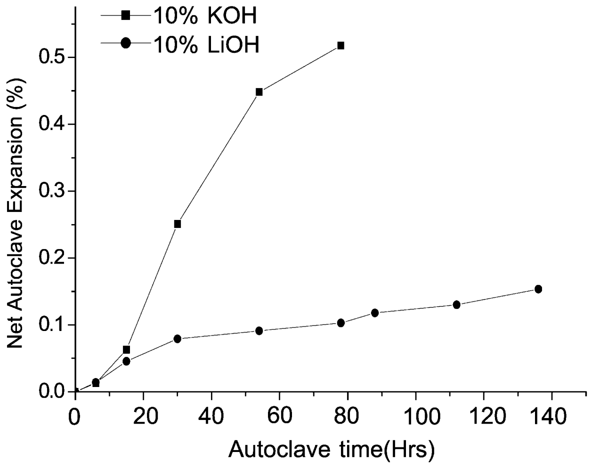
The net AAR expansions of rock prisms JH1 are shown in Fig. 4b. Rock prisms JH1 soaked in 10% LiOH solutions also expanded steadily. It showed a larger expansion in 10% KOH solutions than in 10% LiOH solutions. This may be due to a rapid ACR or to overlapping effect of ACR and ASR.

3.2. Solid products due to lithium hydroxide–dolomite reaction

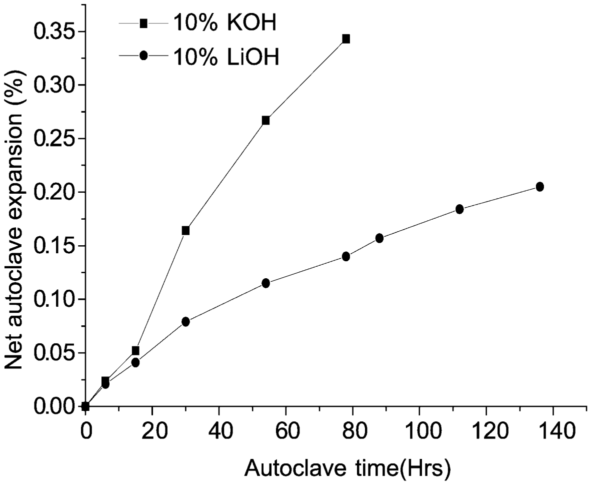
The powder of dolomite TL 2-3 autoclaved either in 10% KOH or LiOH solutions for 6 h at 150 °C was examined by X-ray diffractometer (XRD). The reaction products formed in different alkali solutions are shown in Fig. 5. The solid products of dolomite autoclaved in KOH solutions are brucite and calcium carbonate. It was found that besides these two products, lithium carbonate with new diffraction peaks at 0.415, 0.281 and 0.262 nm also present when dolomite powder was treated in LiOH solutions. Therefore, it is suggested that the phases brucite, calcium carbonate and lithium carbonate would be formed if dolomite reacted with lithium hydroxide. This is somewhat different from the case in KOH solutions.

3.3. Discussions

Because the value of net AAR expansion has deducted both swelling of clays in aggregate and heat-induced expansion of aggregate from the value of gross expansion, it could well avoid the confusion of above factors in understanding ACR mechanism. The aggregate TL2-3 is a nearly pure dolomite. Evidently, its net AAR expansion is only attributed to ACR. Qian [24] also observed the cracks that originated from the dedolomitization rim of dolomite TL2-3 in concrete. Therefore, it is reasonable to conclude that a dolomite aggregate with mosaic texture will bring about expansion or even cracking only if reaction time is long enough in KOH solutions.



(a) Concrete microbars



(b) Rock prisms

Fig. 4. Net AAR expansion of argillaceous dolomite aggregate JH1 in alkali solutions (150 °C).

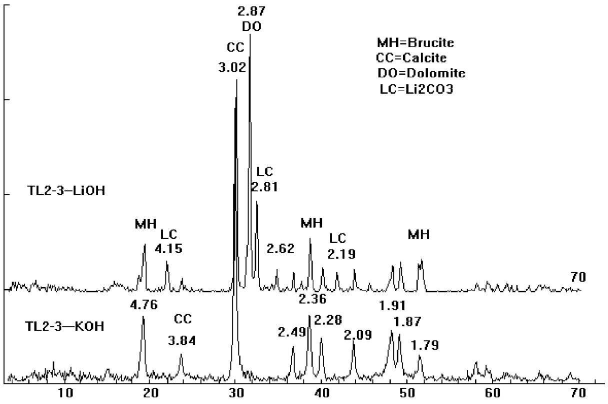


Fig. 5. XRD patterns of dolomite powder autoclaved for 6 h at 150 °C in different alkali solutions.

Meanwhile, a conclusion can be drawn that lithium hydroxide not only suppress the expansion of ASR but also may induce the expansion of ACR. This duplex effect can be used for exploring what mechanism should be responsible for the expansion of aggregates in alkali solutions. The concrete microbars containing the aggregate CK would not expand in LiOH solutions if cryptocrystalline or microcrystalline quartz hidden in the argillaceous matrix of this aggregate were the only reactive components and the only reason for AAR expansion. However, concrete microbars with this aggregate did expand in the LiOH solutions and the net AAR expansions of the specimens increased with autoclave time. Therefore, ACR mechanism rather than ASR mechanism should be responsible for AAR expansion of the aggregate CK.

Based on XRD analysis, dedolomitization reaction of dolomite in LiOH solutions may be written as follows:

$$\mathrm{CaMg(CO_3)_2 + 2LiOH \rightarrow Mg(OH)_2 + CaCO_3 + Li_2CO_3}$$

This process differs from that in KOH solutions in two aspects. Firstly, Li_2CO_3 is deposited as a solid product because Li_2CO_3 has little solubility of 7.2 g/l at 100 °C compared to a solubility of 1560 g/l for K_2CO_3 [25]. Secondly, because of Li_2CO_3 disposition, the dedolomitization process in LiOH solutions becomes a solid volume-increasing reaction. The net volume of solid phases is increased by 48.87%, while the dedomitization of dolomite in KOH solutions was a solid volume reduction process.

Despite these two differences, the mechanism responsible for ACR expansion should be the same. Tang et al. [5] argued that the expansion due to ACR is caused by the growth and rearrangement of dedolomitization products in a confined space, and that the degree of expansion was proportional to the amount of solid products formed [26]. The larger the amount of solid products formed, the larger ACR expansion. For this reason, an important key to control the expansion behavior of ACR is the amount of solid products formed in the dedolomitization process, which depends on both the dedolomitization rate and the reaction course. According to periodic table of element, the alkalescence of LiOH is lower than that of KOH. As a result, reaction rate of dedolomitization of dolomite in LiOH solutions would be expected lower than that in KOH solutions. Meanwhile, more solid products of dedolomitization should form in LiOH solutions than that in KOH solutions if the degree of dedolomitization is the same. It is the directional filling of dedolomitization products from Lithium–dolomite reaction in the confined space that leads to ACR expansion of aggregate. However, the relations between the magnitude of expansion and dedolomitization process in LiOH and KOH should be explored in detail.

4. Conclusions

(1) Lithium hydroxide can effectively suppress ASR expansion and induce ACR expansion. It is the duplex effect of lithium hydroxide that could be used for exploring the mechanism responsible for the expansion of dolomite-bearing aggregates in alkali solutions.

(2) AAR expansion of argillaceous dolomite limestone CK with a typical texture from Kingston, Ontario, Canada, is caused by ACR rather than by ASR.

(3) Some argillaceous dolomite limestones exhibit both ACR and ASR.

(4) When lithium hydroxide is reacted with dolomite, the solid dedolomitization products are brucite, calcium carbonate and lithium carbonate, with a consequent volume increase.

Acknowledgments

This project 59672021 was financially supported by the National Natural Science Fund of China.

References

[1] J.E. Gillott, Mechanism and kinetics of expansion in the alkali–carbonate rock reaction, Can. J. Earth Sci. 1 (1964) 121–145.

[2] D.W. Hadly, Alkali reactivity of carbonate rocks—expansion and dedolomitization, Highw. Res. Board, Bull. 40 (1961) 463–474.

[3] W.C. Sherwood, H.H. Newlon, Studies on the mechanisms of alkali–carbonate reaction, Highw. Res. Rec. 45 (1964) 41–46.

[4] E.G. Swenson, J.E. Gillott, Alkali carbonate reaction, Highw. Res. Rec. 45 (1964) 21–40.

[5] M.S. Tang, Z. Liu, S.F. Han, Mechanism of alkali–carbonate reaction, Proceedings of the 7th International Conference on Alkali–Aggregate Reaction, Noyes Publication, Park Ridge, NJ, USA, 1987.

[6] T. Katayama, Critical review of carbonate reactions—is their reactivity useful or harmful, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction in Concrete, The Concrete Society, London, UK, 1992, pp. 508–517.

[7] T. Katayama, A review of alkali–aggregate reactions in the Asian region—recent topics and future research, Proceedings of East Asia Alkali–Aggregate Reaction Seminar, Tottori, Japan, Supplementary Papers, A33-A43.

[8] M. Regound, Products of reaction and petrographic examination, Proceedings of the 8th International Conference on Alkali–Aggregate Reaction, Elsevier Applied Science, London, 1989.

[9] C.A. Roger, Evaluation of the potential for expansion and cracking due to alkali carbonate reaction, Cem., Concr., Aggregates 8 (1986) 13–23.

[10] J.E. Gillott, Petrology of dolomitic Limestones, Kingston, Ontario, Canada, Geol. Soc. Am. Bull. 74 (1963) 759–778.

[11] B. Fournier, M.A. Berube, Alkali-reactivity potential of carbonate rocks from the St. Lawrence lowlands, Quebec, Canada, Proceedings of the 8th International Conference on Alkali–Aggregate Reaction in Concrete, Japan, Elsevier Applied Science, London, 1989.

[12] W.J. French, The characterization of potentially reactivity aggregates, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction in Concrete, The Concrete Society, London, UK, 1992, pp. 338–346.

[13] L. Tong, M.S. Tang, Concurrence of alkali–silica and alkali–dolomite reaction, Proceedings of the 10th International Conference on Alkali–Aggregate Reaction in Concrete, Melbourne, CSIRO, Australia, 1996.

[14] W.J. McCoy, A.G. Caldwell, New approach to inhibiting alkali–aggregate expansion, J. Am. Concr. Inst. 22 (1951) 693–706.

[15] M. Lawrence, H.F. Vivian, The reactions of various alkalis with silica, Aust. J. Appl. Sci. 12 (1961) 96–103.

[16] Y. Sakaguchi, M. Takakura, A. Kitagawa, H. Takahiro, F. Tomosawa, A. Michihiko, The inhibition effect of Lithium compounds on alkali–silica reaction, Proceedings of the 8th International Conference on Alkali–Aggregate Reaction (1989) 229–234.

[17] D.C. Stark, Lithium admixtures—an alternative method to prevent expansive alkali–silica reactivity, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction, vol. 2. Concrete Society, London (1992) 1017–1025.

[18] S. Diamond, S. Ong, The mechanisms of lithium effects on ASR, Proceedings of the 9th International Conference on Alkali–Aggregate Reaction, vol. 1. Concrete Society, London (1992) 169–278.

[19] E.G. Swenson, J.E. Gillott, Characteristics of Kingston carbonate rock reaction, Highw. Res. Board, Bull. 275 (1960) 18–31.

[20] H. Wang, J.E. Gillott, Alkali–carbonate reaction: significance of chemical and mineral admixtures, Mag. Concr. Res. 47 (1995) 69–75.

[21] NF P18-588-91, Aggregates—Dimensional stability test in alkali medium–accelerated Mortar MICROBAR test, Normalisation Francaise, 1991.

[22] M.S. Tang, X.H. Lan, S.F. Han, Autoclave method for identification of alkali reactive carbonate rocks, Cem. Concr. Compos. 16 (1994) 163–167.

[23] M.S. Tang, S.F. Han, S.H. Zheng, A rapid method for identification of reactivity of aggregate, Cem. Concr. Res. 13 (1983) 417–422.

[24] G.R. Qian, Textural and geological characteristics of carbonate rock and alkali carbonate reaction, PhD thesis, Nanjing Institute of Chemical Technology, China, 1999.

[25] C.W. Robert, J.A. Melvin, H.B. William, CRC Handbook of Chemistry and Physics, B-105, 64th ed., CRC Press, Boca Raton, FL, 1983.

[26] L. Tong, M.S. Tang, Correlation between reaction and expansion of alkali–carbonate reaction, Cem. Concr. Res. 25 (1995) 470–476.