Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 36 (2006) 1191–1200

Cement and Concrete Research

Alteration of alkali reactive aggregates autoclaved in different alkali solutions and application to alkali-aggregate reaction in concrete (II) expansion and microstructure of concrete microbar

Duyou Lu [a,*], Laibao Mei [a], Zhongzi Xu [a], Mingshu Tang [a], Xiangyin Mo [b], Benoit Fournier [c]

[a] College of Materials Science and Engineering, Nanjing University of Technology, 5 New Model Road, Nanjing, 210009, China
[b] Analysis and Test Central, Nanjing Normal University, 122 Ninghai Road, Nanjing, 210097, China
[c] ICON/CANMET, Natural Resources Canada, 405 Rochester Street, Ottawa, ON, Canada K1A 0G1

Received 11 November 2005; accepted 12 January 2006

Abstract

The effect of the type of alkalis on the expansion behavior of concrete microbars containing typical aggregate with alkali–silica reactivity and alkali–carbonate reactivity was studied. The results verified that: (1) at the same molar concentration, sodium has the strongest contribution to expansion due to both ASR and ACR, followed by potassium and lithium; (2) sufficient LiOH can completely suppress expansion due to ASR whereas it can induce expansion due to ACR. It is possible to use the duplex effect of LiOH on ASR and ACR to clarify the ACR contribution when ASR and ACR may coexist. It has been shown that a small amount of dolomite in the fine-grained siliceous Spratt limestone, which has always been used as a reference aggregate for high alkali–silica reactivity, might dedolomitize in alkaline environment and contribute to the expansion. That is to say, Spratt limestone may exhibit both alkali–silica and alkali–carbonate reactivity, although alkali–silica reactivity is predominant. Microstructural study suggested that the mechanism in which lithium controls ASR expansion is mainly due to the favorable formation of lithium-containing less-expansive product around aggregate particles and the protection of the reactive aggregate from further attack by alkalis by the lithium-containing product layer.

Keywords: Alkali-aggregate reaction (C); Alkali–silica reaction; Alkali–carbonate reaction; Lithium compounds (D); Microstructure (B)

1. Introduction

Spratt siliceous limestone (SL) produced in Spratt quarry near Ottawa, Canada and Pittsburg argillaceous dolomitic limestone (PL) produced in Pittsburg quarry, Kingston, Canada are representative examples of aggregate with high alkali–silica reactivity and alkali–carbonate reactivity. Part I of the paper [1] investigated the alteration of the two typical aggregates autoclaved in different alkaline solutions with same molar concentration. NaOH showed the strongest attack on both SL and PL, whereas the weakest attack was with LiOH. For PL, dedolomitization of dolomite obviously occurred in three different alkaline solutions. At the same time, the small amount of quartz in PL was also involved in reaction with alkali solutions. On the other hand, in addition to massive products from alkali–silica reaction, small amount of dolomite that existed in SL seemed also to be dedolomitized under long time autoclaving. For developing accelerating testing method for alkali reactivity of aggregates and testing method to classify ASR and ACR for dolomite-bearing aggregate, the effect of NaOH, KOH and LiOH all at the same molar concentration on the expansion of concrete microbars with SL and PL was studied. This part reports the expansion behaviors of concrete microbars containing SL and PL cured in different alkali solutions. Expansion behaviors of concrete microbar containing zeolitized perlite autoclaved in

Table 1
Chemical composition of limestone

Sample	CaO	MgO	Acid insoluble residue
PL	40.25	6.63	10.90
SL	45.12	2.79	10.07

---

* Corresponding author.
E-mail address: duyoulu@njut.edu.cn (D. Lu).

0008-8846/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2006.01.012

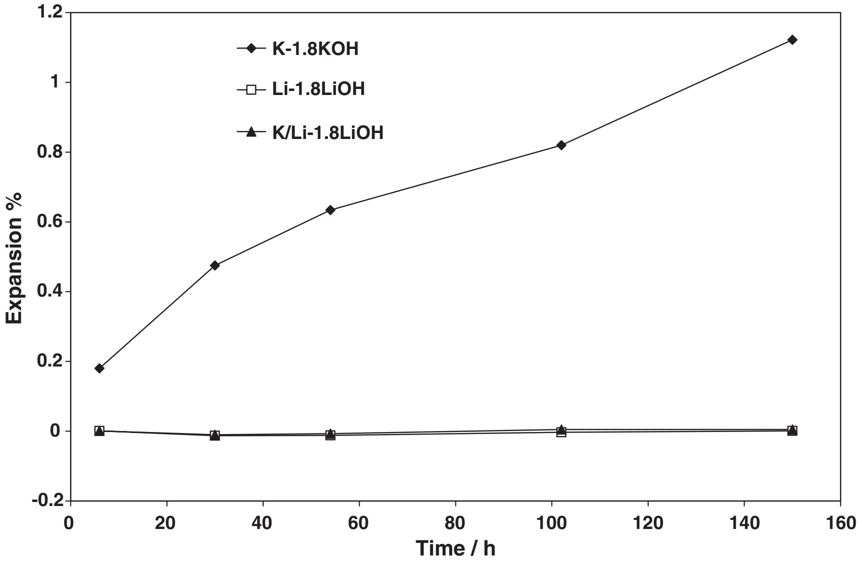

Fig. 1. Autoclave expansion of concrete microbars with zeolitized perlite at 150 °C.

different alkali solutions were also studied for comparison. Microstructure of concrete microbar containing zeolitized perlite was studied to explore the preventive mechanism of lithium against expansion due to ASR.

2. Materials and experimental

2.1. Cement

A low alkali Portland cement that has been used as reference cement in testing alkali reactivity of aggregate in China was used. The chemical composition of the cement is as follows: CaO 64.6%, SiO_2 22.1%, Al_2O_3 4.76%, Fe_2O_3 3.28%, MgO 0.82%, Na_2O 0.07%, K_2O 0.59%, and LOI 0.91%. Specific surface area of the cement is 360 m^2/kg.

2.2. Reactive aggregates

Three well-known alkali reactive aggregates were used in this study. In addition to SL and PL, zeolitized perlite from Shandong, China, which is a high alkali–silica reactive aggregate and is often used as a reference aggregate in China was also used. It consists mainly pearl-like glass matrix and some chalcedony. The chemical composition of SL and PL is listed in Table 1.

2.3. Expansion test

The concrete microbar test method [2] after a small modification was used to evaluate the expansion of aggregates. The aggregates used were crushed to 5–10 mm. Six concrete microbars of 20 × 20 × 60 mm in size were cast with cement

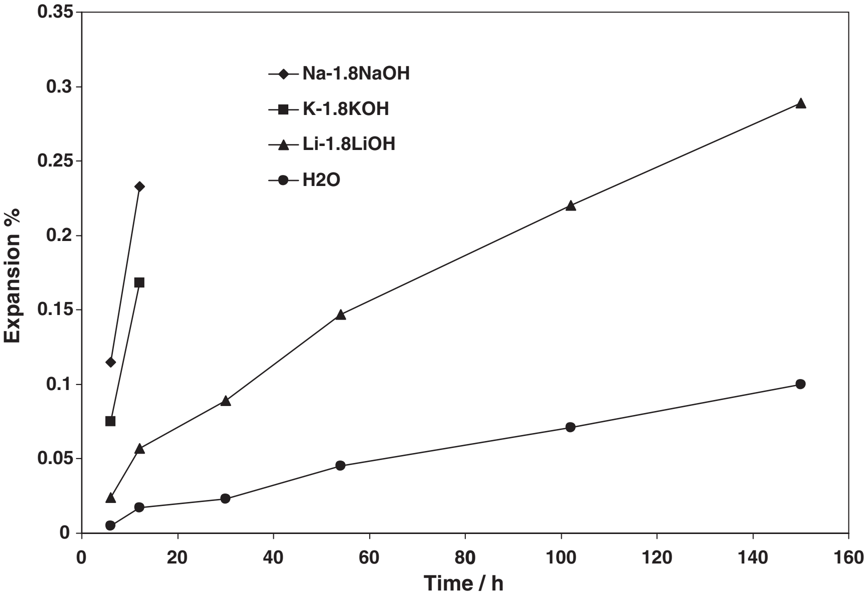

Fig. 2. Autoclave expansion of concrete microbars with Pittsburg limestone at 150 °C.

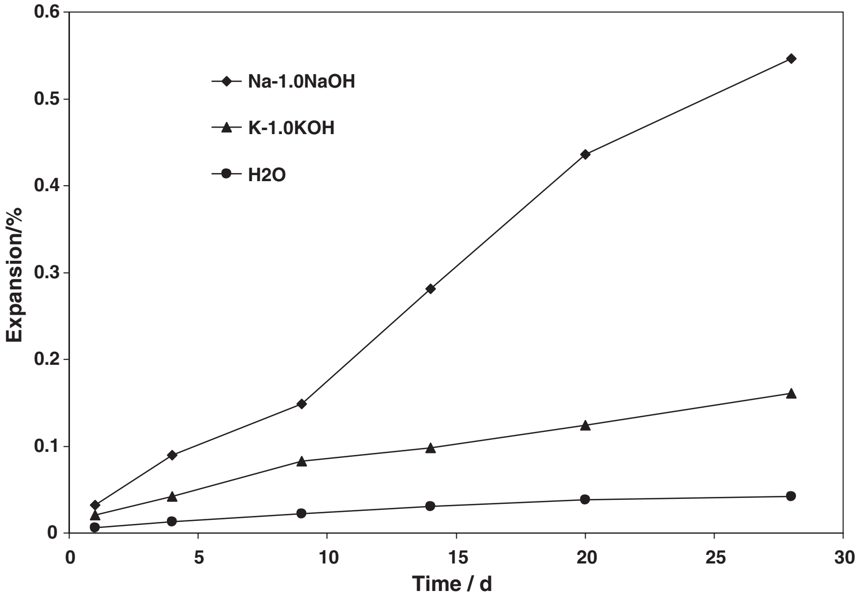

Fig. 3. Expansion of concrete microbars with Pittsburg limestone at 80 °C.

aggregate ratio of 1.0 and W/C ratio of 0.32. For comparison, KOH, NaOH and LiOH were used, respectively, to adjust the cement alkali content to 1.5% Na_2Oe by the addition of them into the mixing water. The bars were removed from the molds after 1-day curing in moist chamber and then steamed at 100 °C for 4 h, then the initial length of bars was measured at room temperature. The bars were then autoclaved at 150 °C or cured at 80 °C for different periods of time in different alkali media. The type of alkali used in curing solution corresponds to that used in concrete bars. In order to compare with previous results, concentration of soaked solution for autoclave is 1.8 $mol \cdot L^{-1}$ (corresponding to 10% KOH in mass), 1.0 $mol \cdot L^{-1}$ alkali solution was used for 80 °C curing. The specimens were extracted from the curing solution after different periods of time. The length change was measured after the bars had cooled down to room temperature and the linear expansions of specimens were calculated. The expansion of one specimen is the average of six bars. For reference, concrete microbars with SL and PL were also made with low alkali cement (0.46% Na_2Oe) without addition of alkali and cured in water at 150 or 80 °C.

2.4. Microstructure of concrete microbar containing zeolitized perlite

Microstructure of concrete microbar containing zeolitized perlite was studied in order to explore the mechanism with

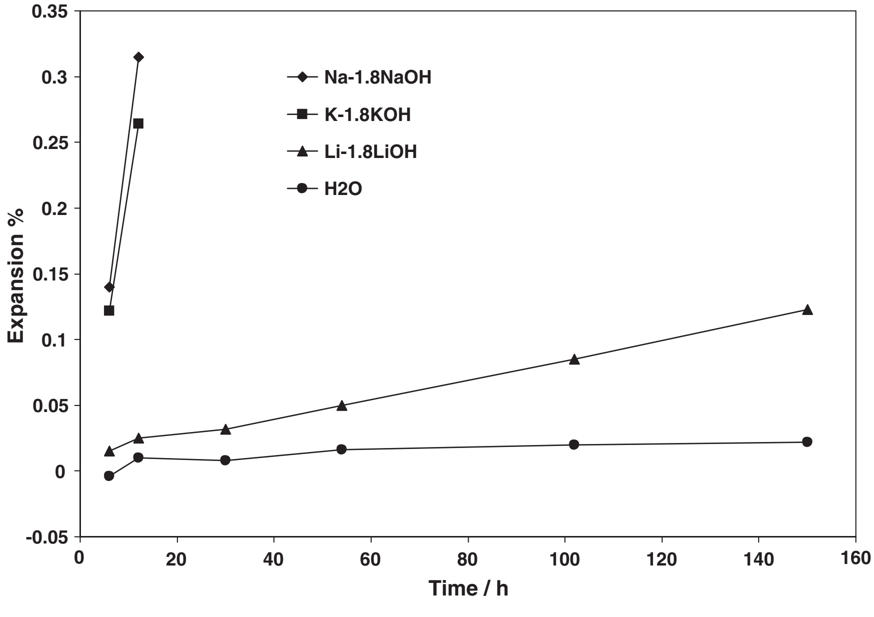

Fig. 4. Autoclave expansion of concrete microbars with Spratt limestone at 150 °C.

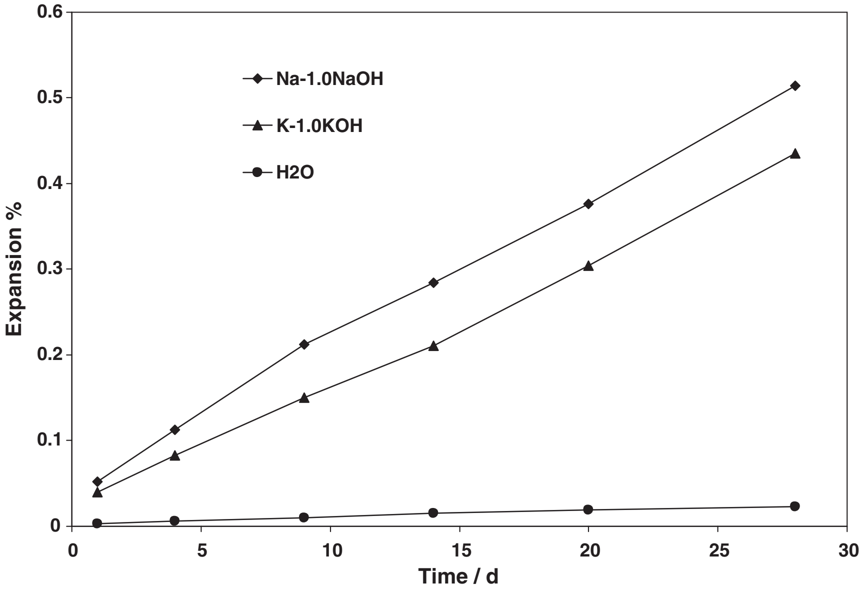

Fig. 5. Expansion of concrete microbars with Spratt limestone at 80 °C.

which LiOH controls expansion due to ASR. Petrographic microscope was used to examine the thin sections of concrete bar containing zeolitized perlite. SEM/EDS were used to examine the morphology and elemental composition of products formed in different specimen. Concrete microbars containing zeolitized perlite examined by SEM/EDS were oven dried at 80 °C for 24 h after autoclaved at 150 °C for 150 h. Fractured surface of concrete microbars was prepared and gold-coated. The microstructure of the specimens was examined by JEOL-5900 SEM combined with Thermal Noran DSI Energy Dispersive Spectrometer (EDS). Secondary electron detector was used to acquire SEM images. Elemental compositions of products with different morphologies were calculated by using semi-quantitative program (standardless method). The parameters of the SEM and EDS were set up as following: an accelerating voltage of 20 KV, an acquisition time of 100 s, the dead time of the EDS detector was below 15%.

2.5. Symbols for specimens

K–1.8 KOH means using KOH to adjust cement alkali content to 1.5% Na_2Oe and storaging in 1.8 M KOH solution; the same rule was with Na–1.0 NaOH and Li–1.8 LiOH.

For zeolitized perlite, K/Li–1.8LiOH means using KOH to adjust cement alkali content to 1.5% Na_2Oe, but putting LiOH with Li / Na molar ratio of 1.0 in the cement and storaging the specimen in 1.8 M LiOH solution.

3. Result and discussion

3.1. Expansion of zeolitized perlite

Fig. 1 shows the expansion of concrete microbar with zeolitized perlite autoclaved in different media. Guangren [3] confirmed concrete microbar with zeolitized perlite developed negligible autoclave expansion (0.04% at 78 h) in 10% LiOH solution (4.17 $mol \cdot L^{-1}$) even with cement alkali content being adjusted to 1.5% Na_2Oe with KOH. Fig. 1 indicates that zeolitized perlite concrete microbars developed smaller expansion or even shrinkage when they were autoclaved in 1.8 $mol \cdot L^{-1}$ LiOH solution, with cement alkali content being enhanced to 1.5% Na_2Oe by addition of LiOH (ZP–LL) or increasing cement alkali content with KOH but putting LiOH with 1.0 Li / Na molar ratio (ZP–KL). It further verified the previous result that sufficient LiOH can successfully suppress expansion due to pure ASR [3,4].

3.2. Expansion of PL

Pittsburg argillaceous dolomitic limestone is a typical aggregate with alkali–carbonate reactivity. The alkali–carbonate reactivity has been proven by a number of results [5,6].

Figs. 2 and 3 are expansion curves of concrete microbars made with Pittsburg limestone in different media and at 150 and 80 °C, respectively. When autoclaved in NaOH or KOH

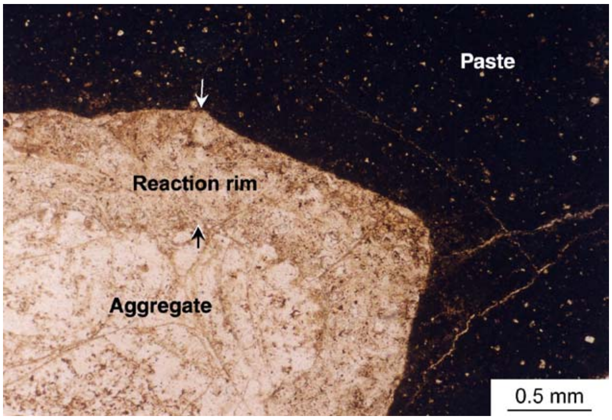

Fig. 6. Petrographic micrograph of ZP–K–1.8 KOH autoclaved for 150 h, polarized light.

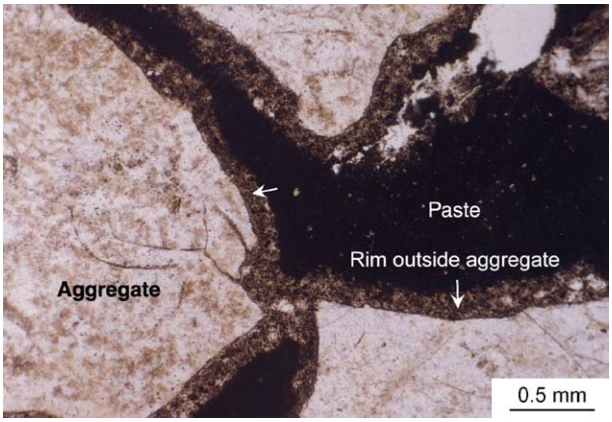

Fig. 7. Petrographic micrograph of ZP–Li–1.8 LiOH autoclaved for 150h, polarized light.

solution at 150°C (Fig. 2), the aggregate showed much higher expansion in NaOH and KOH than in LiOH environments. Different from that of Spratt limestone, it also showed a relative high expansion when autoclaved in LiOH and water environment.

For microbar made with Pittsburg limestone cured in different media at 80°C, as shown in Fig. 3, in addition to stronger activation of NaOH than KOH on ACR expansion, the difference in this activation varies greatly with prolong curing time, especially in later period. A little higher expansion for specimen stored in water was also found.

The relatively high expansion in water of concrete microbar made with PL and low alkali cement may due to several factors, such as swelling of clay minerals in the aggregate by absorbing water, the irreversible heat-induced expansion of aggregate. The ACR may also play an important role because ACR can take place at a relative lower pH [7], with the prolonging of autoclave time, certain extent of dedolomitization might possibly have occurred in PL even with low alkali cement autoclaved in pure water. The net expansion by subtracting expansion of specimen autoclaved in pure water can reasonably be used as an indictor of expansion due to pure AAR.

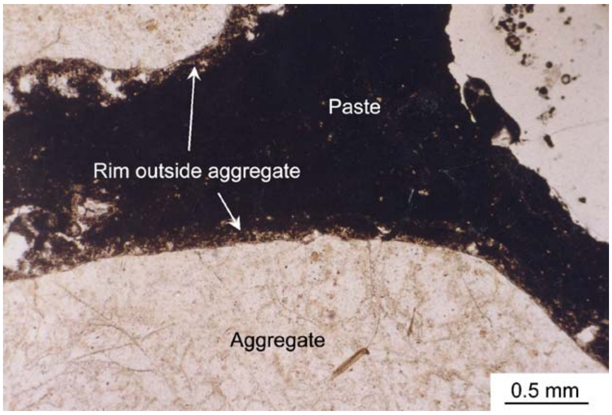

Fig. 8. Petrographic micrograph of ZP–K/Li–1.8 LiOH autoclaved for 150h, polarized light.

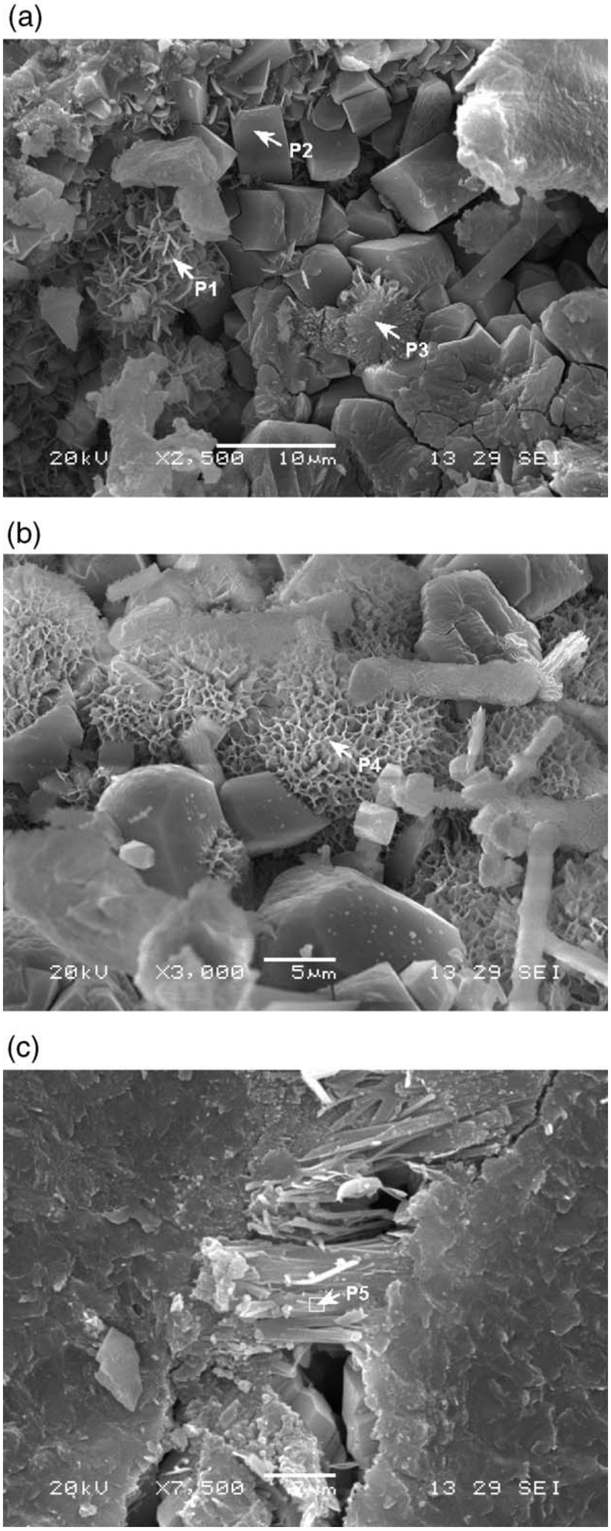

Fig. 9. SEM images ZP–KK autoclaved for 150h (a); (b) product formed beside aggregate; (c) product formed inside aggregate.

The net expansion in LiOH reached 0.189% at 150h, it is reasonable to attribute the expansion to ACR since the expansion due to ASR in PL, if there has, can be completely suppressed by sufficient LiOH both in specimen and solution.

Table 2
Chemical composition of product formed in ZP–KK

	P1	P2	P3	P4	P5
Na_2O	1.31	0.13	2.04	2.14	0.06
Al_2O_3	7.53	16.94	6.33	8.13	11.35
SiO_2	58.03	66.15	58.78	58.27	61.63
K_2O	20.18	16.43	19.24	20.62	21.18
CaO	12.95	0.35	13.61	10.87	5.78

3.3. Expansion of SL

Autoclave expansion of concrete microbars made with SL at 150 °C in 1.8 mol·L^{-1} NaOH, KOH, LiOH solutions and water is shown in Fig. 4. Expansion develops rapidly both in NaOH and KOH solution under autoclave conditions. The 6 h expansions in NaOH and KOH were 0.140% and 0.122%, respectively, and they reached 0.315% and 0.264% after 12 h. It indicates that at the same OH^- level, NaOH can induce larger ASR expansion than KOH. The results also suggest that Spratt limestone is high reactive aggregate in alkali solution and autoclave concrete bar result correlate well with Accelerated Mortar Bar Test (AMBT, ASTM C1260), the 14d and 28d mortar bar expansion are 0.391% and 0.617%, respectively. The reference bar made with low alkali cement and autoclaved in water developed negligible expansion during the whole autoclave period, it suggests there was no remarkable heat-induced expansion in Spratt limestone due to the very fine calcite and no obvious ASR expansion with low alkali cement. It is worthy to notice that microbar with added LiOH and soaked in LiOH solution also expanded when prolong autoclave time, and it reached 0.123% at 150 h. The net expansion by deducing the expansion in water is over 0.1% at 150 h.

As shown in Fig. 5, almost a linear increase in expansion with prolong time and a stronger activation of sodium than that of potassium was also observed when the concrete microbars were cured at 80 °C in NaOH and KOH solution with 1 mol·L^{-1}. The difference in the activation on expansion between sodium and potassium increases with time at early period, it then almost keeps stable in later period. Similar to that autoclaved at 150 °C, there was no obvious expansion either in specimen soaked in water.

It was confirmed both in laboratory and field that LiOH can successfully control ASR expansion when sufficient lithium existed [3,4,8–13], the above result with zeolitized perlite also verified that for aggregate with pure alkali–silica reactivity, such as zeolitized perlite, it did not expand in LiOH environment, even with KOH added in the matrix. It suggested that other mechanism than ASR might be responsible for the expansion of SL in LiOH. The SL used contains 2.79% MgO, that is approximately 13% of dolomite in the rock (assuming all MgO was from dolomite) and the dedolomitization of dolomite in SL was detected by XRD and SEM/EDS after being autoclaved in LiOH solution [1]. Since the expansion due to swelling of clays and irreversible thermal shock can be reasonably subtracted by deducting expansion of bars autoclaved in pure water, it is reasonable to attribute the expansion of SL in LiOH to ACR. The above results indicated that Spratt limestone, which is often recognized as typical aggregate with alkali–silica reactivity, also expanded in the environment with sufficient LiOH. It suggested that in addition to alkali–silica reactivity, which is the main contribution to its expansion, there might be also some extent of alkali–carbonate reactivity in this aggregate, i.e. it can exhibit both ASR and ACR reactivity.

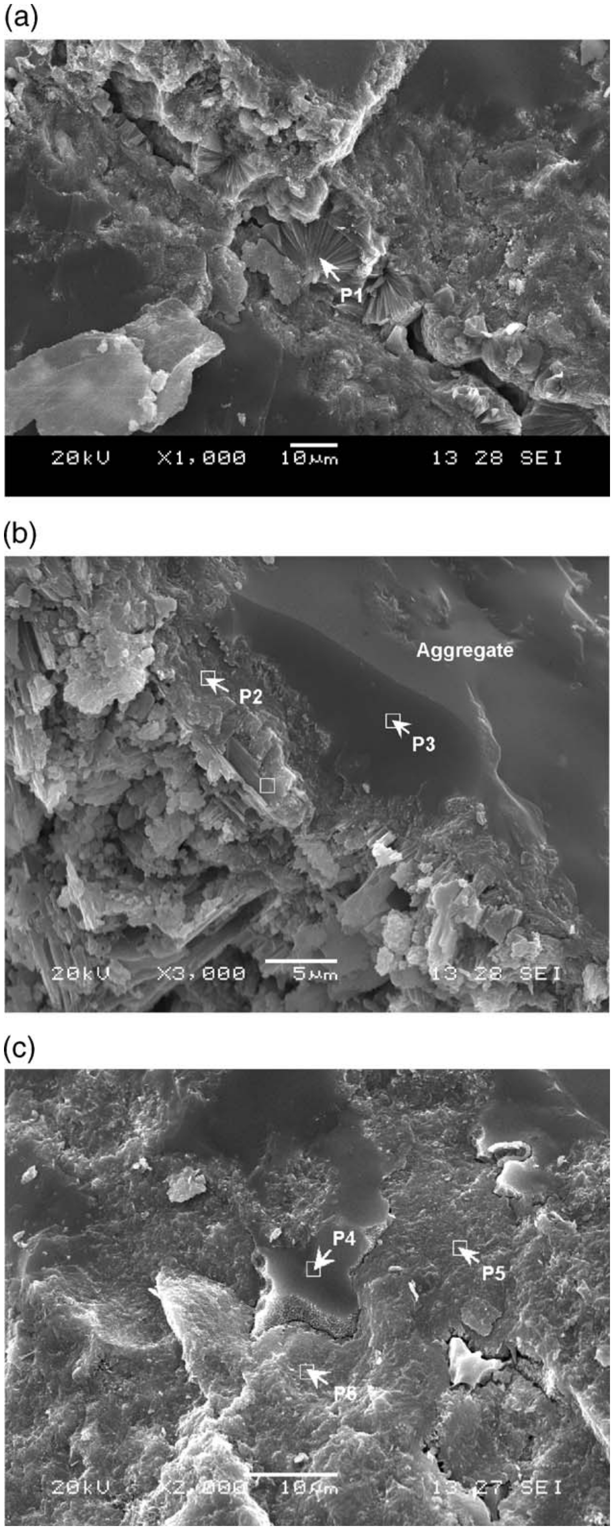

Fig. 10. SEM images of ZP–LL autoclaved for 150 h. (a) Crystals formed inside aggregate; (b) gel formed around aggregate; (c) gel formed inside aggregate.

Table 3
Chemical composition of denoted points in ZP–LL

	P1	P2	P3	P4	P5
Na_2O	0.62	0.39	2.44	1.66	–
Al_2O_3	2.5	5.31	11.25	12.20	8.67
SiO_2	96.17	85.92	81.96	80.91	89.03
K_2O	0.32	0.21	2.28	3.22	0.19
CaO	0.40	8.17	2.06	2.02	2.11

From part 1 of the paper [1] and above results, it indicated that at the same OH^- concentration, sodium has greater activation on AAR and its expansion than potassium. While lithium has duplex effect on ASR and ACR, that is it can induce ACR and inhibit ASR. NaOH and KOH are commonly used in testing alkali reactivity of aggregate. Limiting the total alkali content in concrete has been a common measure to avoid the AAR. Total alkali in fly ash has also been considered as one of the most important parameters that affect the effectiveness of fly ash in controlling ASR expansion. The result from this paper suggests that, in addition to the total alkali content in concrete, attention should also be paid to the type of alkalis in the system due to their different effect on AAR.

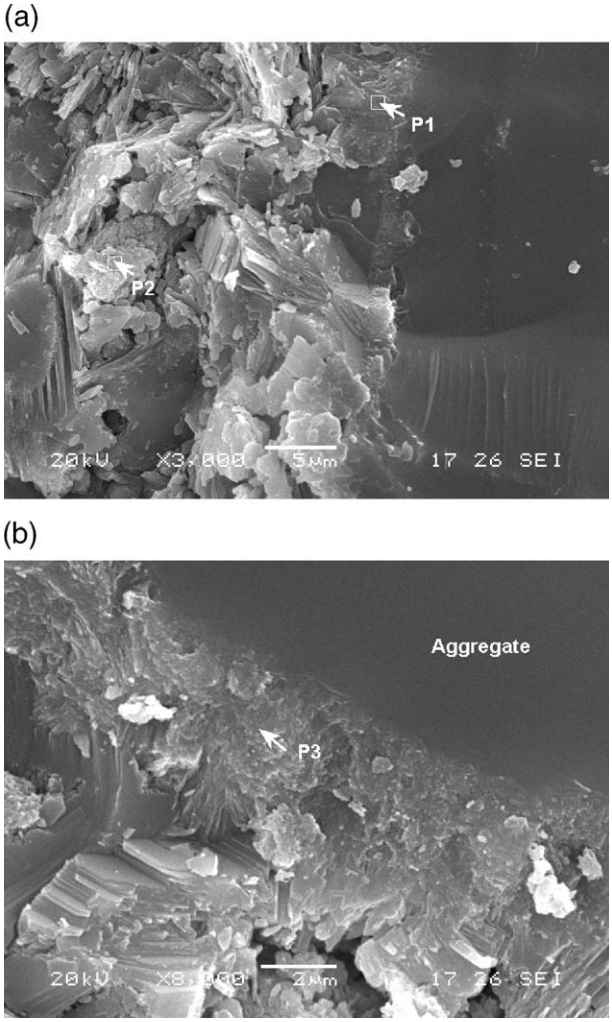

Fig. 11. SEM images of ZP–KL autoclaved for 150h.

Table 4
Chemical composition of product in ZP–KL

	P1	P2	P3
Na_2O	0.44	–	0.57
Al_2O_3	5.80	0.9	6.45
SiO_2	80.81	19.68	83.20
K_2O	0.09	–	0.03
CaO	12.86	79.42	9.75

3.4. Microstructural study of concrete microbar with zeolitized perlite

3.4.1. Thin section examination

For ZP–K–1.8 KOH, cement alkali was adjusted by addition of KOH and autoclaved in KOH solution. The aggregate particles were severely attacked by alkalis after autoclaving for 150h. Microcracks developed extensively both in aggregate particles and in the surrounding paste. Due to the high reactive glass and pearl-like cracking in the glass matrix of the aggregate, it developed a relative wide reaction rim inside the aggregate particle, as shown in Fig. 6, which had a dark brown tone compared with the bright color of the inner side of the particle. For specimen autoclaved in LiOH solution, no matter whether KOH was added to the cement or not, the reaction rim also developed around the aggregate, but it was not inside but outside the aggregate particles. Furthermore, the edge of the aggregate (interface between aggregate and reaction rim) was clear, suggesting the surface of aggregate was not significantly affected. The photos of ZP–Li–1.8 LiOH and ZP–K/Li–1.8 LiOH are shown in Figs. 7 and 8. Under crossed polarized light, the product rim around aggregate was transparent suggesting the rim was consisted of crystalline materials.

3.4.2. SEM/EDS examination

3.4.2.1. ZP–K–1.8 KOH. Fig. 9 shows the SEM images of concrete bar with zeolitized perlite autoclaved in 1.8M KOH solution. ASR product with typical morphologies reported in literatures can be easily observed beside aggregate particles. Blade, rosette, and prismatic crystals and radiating gel were shown in Fig. 9a and b. Since the aggregate contains a lot of pearl-like cracks in the glass matrix, which can act as fast access path to alkalis in pore solution, ASR product can also easily form inside aggregate [14], crystal agglomerates can be observed in cracks inside the aggregate (Fig. 9c). EDS results shown in Table 2 indicated all products formed beside (P1–P4) and inside aggregate (P5) have a very high alkali content. Blade, rosette crystals (P1, P4) and radiating gel (P3) have similar elemental composition, suggesting these crystals were transformed from the ASR gel at later period. Prismatic crystal (P2) and agglomerate formed inside aggregate (P5) have a relative high aluminum and silica content with a lower calcium content, which may suggest that, before crystallization, they are less expansive than typical ASR gel.

It was generally considered that crystalline ASR product was transformed at later period and has little contribution to further expansion, since it was often found in the void adjacent to

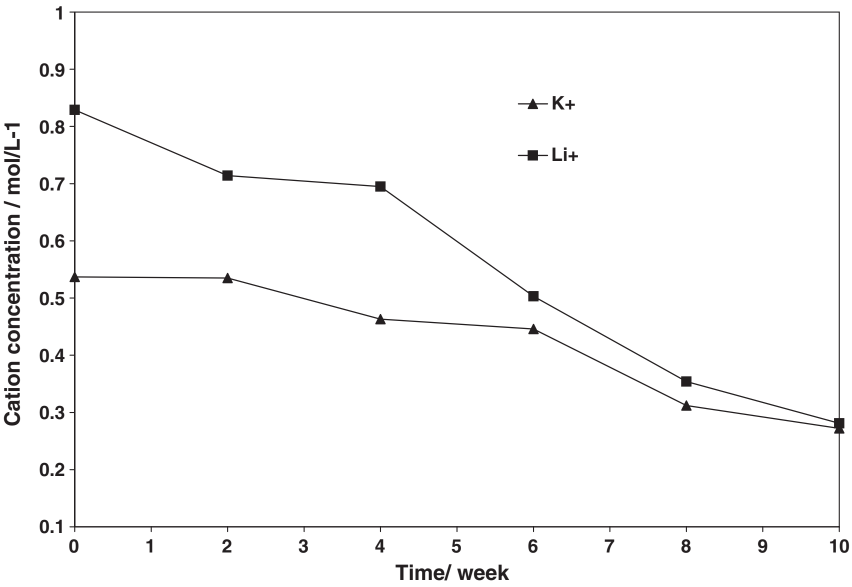

Fig. 12. Variation of Li and K ions concentration in the mixture of LiOH and KOH with silica glass at 80 °C.

reactive aggregate, where there was enough space for the growth of crystals. It was not clear whether the orientated growth of massive crystals inside aggregate have contributed to the expansion of aggregate at later period.

3.4.2.2. ZP–Li–1.8 LiOH. Fig. 10 shows some typical images of ZP–Li–1.8 LiOH autoclaved for 150 h. It was clearly demonstrated that the aggregate was involved in the reaction with LiOH both inside and around the aggregate. Fig. 10a and c shows the crystal agglomerate and amorphous gel formed inside the aggregate. The edge of aggregate was corroded although it showed a clear interface in thin section under optical microscope and a layer of gel formed as shown in Fig. 10b. EDS results, as shown in Table 3, indicated products formed inside (P1, P5) and around aggregate (P2) had very high SiO_2 content (higher than that in aggregate P3, P4), with very low sodium and potassium content. As expected, gel formed around aggregate had a high CaO content relative to product formed inside aggregate. Lithium cannot be detected by EDS due to the low energy of the X-ray photon of lithium, however, these products probably contained a fair amount of lithium according to the results reported in Part 1 that a fair amount of lithium silicate formed on aggregate surface when the aggregate was autoclaved in LiOH solution.

3.4.2.3. ZP–K/Li–1.8 LiOH. Similar results to ZP–Li–1.8 LiOH were obtained in ZP–K/Li–1.8 LiOH, in which cement alkali content was enhanced to 1.5% Na_2Oe by addition of KOH, whereas LiOH was used in cement by Li/Na molar ratio of 1.0. Gel product, which is rich in silica and possibly lithium and poor in sodium and potassium, was also formed around aggregate as shown in Fig. 11 and Table 4. The very low potassium and sodium content in gel around aggregate suggest that lithium may be more favorable than potassium and sodium in reaction with silica.

3.5. Mechanism of ASR suppression by LiOH

Several hypotheses have been proposed to interpret the effect of lithium compounds on controlling ASR [15], including: (1) formation of stable and less-expansive lithium rich product [4,5,16], and the formation of lithium–silica reaction is more favorable than sodium or potassium–silica reaction [17]; (2) suppression of the rate of silica dissolution [16,18,19], which suggests lithium can limit the expansion by limiting the rate of product formation; (3) decreased repolymerization of dissolved silica [20], which suggests that in addition to decreasing the rate of silica dissolution, lithium may limit repolymerization of dissolved silica species into a gel, effectively reducing the potential for expansion; (4) reduction of the double-layer repulsive forces between colloidal particles within product [21]. The last two hypotheses were proposed based on the principles of colloidal chemistry.

In essence, the mechanisms of controlling ASR expansion in the presence of lithium were focusing on two aspects regardless of the process: modification of the expansive character of ASR product and/or decrease in the rate of silica dissolution resulting a reduced degree of alkali–silica reaction.

The above microstructural results and the findings in Part 1 of this paper indicated that lithium was involved in reaction with silica to form lithium silicate crystal or lithium-containing gel and the reaction degree of aggregate with alkali–silica reactivity in LiOH solution was significantly lower than that in KOH and NaOH solutions with the same molar concentration. It was commonly believed that ASR gel containing certain amount of lithium was essentially non-expansive no matter whatever the mechanisms involved. By measuring the lithium and alkali concentrations in expressed pore solution from mortar bars, Sakaguchi et al. [17] found the concentration of lithium decreased with time, while alkali concentrations remained nearly constant. In the absence of lithium, the alkali concentrations of the expressed pore fluid decreased over time, suggesting that lithium–silica reaction is more favorable than the sodium or potassium–silica reaction in mortar bars [15]. By measuring the lithium and potassium concentrations in model mixed solution of LiOH and KOH with silica glass, Mo [22] also found that both lithium and potassium decreased with time, but lithium was favorable over potassium in reaction with silica, especially at the first two weeks (Fig. 12). Therefore, favorable formation of less-expansive product may be one of the most important reasons that lithium can control ASR. However, the reduced reaction degree of silica or ASR aggregates in LiOH solution may not only due to the decreased rate of silica dissolution in LiOH because, over time, the concentration of dissolved silica for each alkali–hydroxide concentration can approach the same value, independent of alkali type [16], which means that lithium may reduce the rate of dissolution, not the solubility of silica [15]. The findings in Part 1 of this paper and the above SEM/EDS results suggested that the existence of lithium-containing product layer around the particles with alkali–silica reactivity seems very important in protecting the particle from further attack by alkalis, thus resulting a reduced reaction degree of the aggregate.

From above results, the favorable formation of lithium-containing less-expansive product around aggregate and the protection of the reactive aggregate by the lithium-containing product layer from further attack by alkalis are the most important reasons that lithium can control expansion due to ASR.

3.6. Interpretations to existed experimental findings

Based on this hypothesis, several experimental phenomena related lithium protection against ASR, such as threshold lithium dosage, pessimum effect of LiOH and the disconnection between aggregate reactivity and required lithium dosage to control expansion, can be satisfactorily interpreted.

Since both C–S–H and dissolved silica have greater affinity for lithium over sodium and potassium [5,17,22], to form a lithium-containing product layer around aggregate particle, there exists an accordance between the concentrations of lithium ions and dissolved silica as well as alkali ions (sodium and potassium) around particle, especially at early time. Both C–S–H and dissolved silica from aggregate will compete for lithium. It needs a threshold lithium content (or Li/Na molar ratio) to form non-expansive ASR gel. If the lithium concentration is lower than the threshold, it is insufficient to be incorporated in ASR product to change the expansive character.

High alkalinity in paste can reduce the affinity of C–S–H for lithium, while increasing the concentration of dissolved silica around the aggregate, is favorable for the formation of lithium-containing ASR product if sufficient lithium is available. Low alkalinity in paste, however, will form C–S–H with low alkalinity resulting to an increase in the affinity for lithium. On the other hand, low alkalinity in paste is unfavorable for the dissolution of reactive silica, thus reducing the formation of lithium-containing product layer around the aggregate. Therefore, at same Li/Na molar ratio, a better suppressing effect was with high alkali cement than low alkali cement.

The different responses to lithium of aggregates with different alkali–silica reactivity may also be attributed to the competition for lithium between C–S–H and dissolved silica. The reactive constituents in high reactive aggregate, such as chert and zeolitized perlite, are amorphous or very poor crystalline silica and homogenously distributed in the particle, which are easily soluble even with low alkali cement, and thus is favorable for competence reaction with lithium to form non-expansive product around aggregate and resulting a good response to lithium. The reactive constituent in aggregates with low alkali–silica reactivity, however, is mainly microcrystalline quartz, which has a better crystallinity relative to amorphous silica, and is often distributed inhomogenously in aggregate particle, thus it is not favorable to produce sufficient dissolved silica to compete for lithium with C–S–H, especially at early period and when the alkali content in the system is low. At a determined lithium content, it will be insufficient to form lithium-containing non-expansive ASR product at later period due to the uptake of lithium by C–S–H. The inhomogenous distribution of the reactive constituents is not favorable to form a protecting product layer either. At determined Li/Na molar ratio above or equal to the threshold value, the appropriate high alkali content in the system would lead to a better suppressing effect on expansion of aggregate with low alkali–silica reactivity.

4. Conclusions

The effect of the type of alkalis on expansion behavior of concrete microbars containing typical aggregate with alkali–silica reactivity and alkali–carbonate reactivity was studied. The results verify that: (1) at the same molar concentration, sodium has the strongest contribution to expansion due to both ASR and ACR, followed by potassium and lithium; (2) sufficient LiOH can completely suppress expansion due to ASR whereas induce expansion due to ACR. It is possible to use the duplex effect of LiOH on ASR and ACR to clarify the ACR contribution when ASR and ACR may coexist. (3) It has been shown that small amount of dolomite in the fine-grained siliceous Spratt limestone, which has always been used as a reference aggregate with high alkali–silica reactivity, might dedolomitize in alkaline environment and contribute to expansion.

Microstructural study on the concrete microbar containing zeolitized perlite autoclaved in different alkali solutions suggested that the mechanism in which lithium controls ASR expansion is mainly due to the favorable formation of lithium-containing less-expansive product around aggregate and the protection of the reactive aggregate by the lithium-containing product layer from further attack by alkalis.

Acknowledgements

This study was supported by National 973 key project of China, 2001CB610706 and Natural Science Fund from Jiangsu

Provincial Department of Education, 05KJB430046. Thanks also to Dr. Paddy Grattan-Bellew from National Research Council of Canada for his help and suggestions in editing the draft of the paper.

References

[1] Duyou Lu, Laibao Mei, Zhongzi Xu, Mingshu Tang, Benoit Fournier, Alteration of alkali reactive aggregates autoclaved in different alkali solution and application to alkali-aggregate reaction in concrete (I) Alteration of alkali reactive aggregate in alkali solution, 36 (2006) 1176–1190, doi:10.1016/j.cemconres.2006.01.008.

[2] M.S. Tang, X.H. Lan, S.F. Han, Autoclave method for identification of alkali reactive carbonate rocks, Cement and Concrete Composites 16 (1994) 163–167.

[3] Qian Guangren, Min Deng, Mingshu Tang, Expansion of siliceous and dolomitic aggregates in lithium hydroxide solution, Cement and Concrete Research 32 (2002) 763–768.

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

[5] J.E. Gillott, Petrology of dolomitic limestones, Kingston, Ontario, Canada, Bulletin of the Geological Society of America 74 (1963) 759–778.

[6] J.E. Gillott, E.G. Swenson, Mechanism of the alkali–carbonate reaction, Journal of Engineering Geology 2 (1969) 7–23.

[7] Min Deng, Mingshu Tang, Mechanism of dedolomitization and expansion of dolomitic rocks, Cement and Concrete Research 23 (1993) 1397–1408.

[8] S. Diamond, S. Ong, The mechanisms of lithium effects on ASR, Proceedings of 9th International Conference on Alkali-Aggregate Reaction, Proceedings of 9th International Conference on Alkali-Aggregate Reaction, vol. 1, Concrete Society, London, UK, 1992, pp. 269–278.

[9] J.S. Lumley, ASR suppression by lithium compounds, Cement and Concrete Research 27 (1997) 235–244.

[10] B.Q. Blackwell, M.D.A. Thomas, A. Sutherland, Use of lithium to control expansion due to alkali–silica reaction in concrete containing U.K. aggregates, in: V.M. Mahotra (Ed.), Proceedings of 4th International Conference on Durability of Concrete, American Concrete Institute, Detroit, 1997, pp. 649–663, ACI SP-170.

[11] M.D.A. Thomas, R. Hooper, D. Stokes, Use of lithium-containing compounds to control expansion in concrete due to alkali–silica reaction, Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR), Quebec, Canada, 2000, pp. 783–810.

[12] B. Durand, More results about the use of lithium salts and mineral admixtures to inhibit ASR in concrete, Proceedings of the 11th International Conference on Alkali-Aggregate Reaction (ICAAR), Quebec, Canada, 2000, pp. 623–632.

[13] B. Fournier, D.B. Stokes, A. Ferro, Comparative field and laboratory investigations on the use of supplementary cementing materials (SCMs) and lithium-based admixtures to control expansion due to alkali–silica reaction (ASR) in concrete, Proceedings of the 6th International CANMET/ACI Conference on Durability of Concrete, Thessaloniki, Greece, 2003, pp. 823–851.

[14] Duyou Lu, Zhongzi Xu, Mingshu Tang, ASR models of aggregates with different microstructure and texture, Journal of Chinese Ceramics Society 30 (2002) 149–154.

[15] K.J. Folliard, M.D.A. Thomas, K.E. Kurtis, Guidelines for the Use of Lithium to Mitigate or Prevent ASR, Publication No. FHWA-RD-03-047, 2003, 61 pp.

[16] M. Lawrence, H.F. Vivian, The reactions of various alkalis with silica, Australian Journal of Applied Science 12 (1961) 96–103.

[17] . Y. Sakaguchi, M. Takakura, A. Kitagawa, H. Takahiro, F. Tomosawa, A. Michihiko, The inhibition effect of lithium compounds on alkali–silica reaction, in: K. Okada, et al., (Eds.), Proceedings of the 8th International Conference on Alkali-Aggregate Reaction, 1989, pp. 229–234, Kyoto.

[18] P.W.J.G. Wijnen, T.P.M. Beelen, J.W. de Haan, C.P.J. Rummens, L.J.M. van de Ven, R.A. van Santen, Silica gel dissolution in aqueous alkali metal hydroxides studies by 29Si NMR, Journal of Non-Crystalline Solids 109 (1989) 85–94.

[19] C.L. Collins, Examination of the mechanisms by which lithium additives inhibitiong alkali–silica reaction gel expansion, M.S Thesis, 2002, Georgia Institute of Technology, Atlanta.

[20] K.E. Kurtis, P.J.M. Monteiro, Chemical additives to control expansion of alkali–silica reaction gel: proposed mechanisms of control, Journal of Materials Science 38 (2003) 2027–2036.

[21] . M. Prezzi, P.J.M. Monteiro, G. Sposito, Alkali–silica reaction — part 2: the effect of chemical additives, ACI Journal 95 (1998) 3–10 JAN–FEB.

[22] Mo Xiangyin, Long-term effectiveness and mechanism of chemical admixtures in inhibiting alkali–silica reaction, Ph D thesis, 2001, Nanjing University of Technology.