CONTROLLING EFFECT OF LITHIUM NITRITE ON ALKALI-AGGREGATE REACTION

Kazunori Era[1*], Takafumi Mihara[1], Akihiko Kaneyoshi[2], Toyoaki Miyagawa[3]

[1]Kyokuto Co., Ltd. Higashi-ku, HIROSHIMA, Japan

[2]Daitetsu Kogyo Co., Ltd. Yodogawa-ku, OSAKA, Japan

[3]Dept. of Civil and Earth Resources Eng., Kyoto University, Nishikyo-ku, KYOTO, Japan

Abstract

Alkali-aggregate reaction in Japan is mostly alkali silica reaction (ASR). ASR is responsible for cracks in the surface of concrete structures and also causes cracks within concrete and a reduction of the compressive strength and static modulus of elasticity of concrete. Recently, lithium has been spotlighted for repairing deteriorated concrete. This is because lithium-ion has been shown to inhibit the expansion of alkali-silica gel.

Therefore, the authors have developed "The ASR-Lithium Method" to repair concrete structures which have deteriorated from ASR. The ASR-Lithium Method inhibits future ASR expansion through pressurized injections of lithium nitrite supplied inside concrete. As a result of extracting core sample material from concrete structures which underwent this method and conducting tests pertaining to areas such as the permeation range of lithium-ion and the extent of reduction of expansion rate, it was demonstrated that this method was effective in inhibiting ASR expansion.

Keywords: ASR, lithium nitrite, pressurized injection, repair, residual expansion

1 INTRODUCTION

In recent years, reports have been made regarding instances of the fractures of reinforcement bars resulting from expansion of concrete due to alkali-aggregate reaction in Japan, and alkali-aggregate reaction has become a deterioration phenomenon which is causing quite a bit of concern. The alkali-aggregate reaction seen in Japan is mostly alkali silica reaction (referred to as "ASR" hereinafter)[1].

The traditional repair method for ASR has generally focused on methods designed to protect the outer surface with the goal of blockage of water infusion from the exterior. However, among cases where such techniques were applied, it seems that instances exist where sufficient effects were not achieved and deterioration resulted [2], As a consequence countermeasures working on a more fundamental level are being sought. Meanwhile, repair methods using lithium chemical compounds with the goal of inhibiting the expansion of alkali-silica gel are receiving attention. For lithium material, lithium nitrite is mainly used within Japan. To date, methods where lithium nitrite has been applied to concrete surfaces and infused into cracks have been employed. However, it has been pointed out that for such methods, challenges exist such as sufficient surface application and the adequate interior infusion of the amount of lithium-ion required to inhibit ASR. Ion diffusion in the concrete interior also requires a long period of time (about 30mm/year) to achieve proper penetration [3]. As a method for reliably and quickly supplying lithium nitrite into the concrete interior, the authors propose the pressurized injection of lithium nitrite, and have developed the ASR-Lithium Method [4]. This study reports the inspection results of the ASR inhibitory effect for an actual structure for which the ASR-Lithium Method was applied.

2 SUMMARY OF THE ASR-LITHIUM METHOD

Previous research related to inhibition of ASR expansion by lithium compounds focused mainly on experimental research of samples created by these compounds with fresh concrete. Though the results of such research have clarified the inhibitory effect of ASR expansion using lithium, in order to realize such achievements for repair measures of existing concrete structures, there is another hurdle which must be overcome. That is the problem of how to supply lithium-ion to the interior of

* Correspondence to: era@o.kkn.co.jp

hardened concrete. In response to this problem, the authors considered a pressurized injection into the interior of concrete of aqueous solution with a high concentration of lithium chemical compound. As a result, "the ASR-Lithium Method" was developed. Lithium nitrite was chosen as the active lithium compound.

The method of supplying lithium to the concrete interior in the ASR-Lithium Method is pressurized injection. To facilitate this injection holes (the diameter of 20mm) were drilled at 500 mm intervals. The drill depth was approximately 200 mm less the thickness of the concrete member. A 40% lithium nitrite aqueous solution was then injected via pressurized injection through the holes at pressures of 0.5 – 1.5 MPa. It was known that the time necessary for injection is greatly affected by concrete strength or degradation level. According to previous results, about 60 hours was necessary for injection in concrete with compressive strength was 33.3MPa and injection pressure at 1.0MPa [5].

3 EXPERIMENTAL METHOD USED TO INSPECT EFFECT

3.1 Target structure and process specifications

The structures targeted for inspection in this study were a retaining wall A (Figure 3) and B (Figure 4). Both are concrete structures erected in the late 1970s, meaning that approximately 30 years has passed since construction. Noticeable deterioration from ASR, such as hexagonal cracks and white gel deposits, were visible. Aggregate used for both retaining walls was pyroxene andesite, and a reaction ring was observed around the aggregate by optical microscopy of thin sections. The 13 weeks accelerated expansion test in an environment of 40 °C at 95% relative humidity was carried out for cores sampled from both retaining walls. As a result, each residual expansion of retaining wall A and retaining wall B was 0.055% and 0.081%. Ministry of Land, Infrastructure, Transport, and Tourism defined that aggregate which has more than 0.05% residual expansion after 13 weeks cured under the above mentioned conditions should be judged to be injurious or potentially injurious [6]. Therefore both retaining walls were judged to be damaged by ASR and have injurious residual expansion. Treatment was performed repair work on these structures using the ASR-Lithium Method.

The implementation specifications for the ASR-Lithium Method were set based on results of inspecting the concrete core samples extracted from each structure (Table 1). The necessary quantity of lithium nitrite was determined by the quantity of Na^+ in total alkali (total sodium oxide equivalent). In previous researches, it was reported that the necessary Li/Na molar ratio was 0.74 [7] or 0.5 [8] to control ASR expansion. These results were obtained where lithium compounds were mixed in the fresh concrete. Due to the pressure injection method used in this study, because loss or unevenness of lithium ion during injection was expected. Therefore in this study, a necessary Li/Na molar ratio was decided to be 1.0 as a conservative estimate considering uncertainty. The time required for injection was dependant on interactive impact of the extent of deterioration in the concrete, injection pressure, and injection hole interspacing. The time required to complete pressurized injection for each injection is shown on Table 1.

3.2 Quantitative analysis of lithium-ion

In order to inhibit ASR expansion through the proposed method, it was necessary to spread lithium-ion across a wide range within the concrete interior through pressurized injections. In order to quantitatively confirm the distribution of the lithium-ion delivered into the concrete interior, quantitative analysis test was executed for lithium-ion in retaining wall A. One month after completion of pressurized injection, one long core (diameter of 50 mm, the length of 1200 mm) was extracted vertically from the top of the retaining wall (Figure 5) and sliced it in 50 mm intervals. Then we crushed each slice into powder. Using ICP-OES (inductively coupled plasma optical emission spectroscopy), a quantitative analysis of the lithium-ion concentration within the extracted powder sample was performed. In order to extract lithium-ion from a powder sample, acid digestion (HCl, $HClO_4$) of the sample was performed. This test allowed us to confirm whether or not an amount of lithium-ion equivalent to the amount required to inhibit ASR was distributed sufficiently within the concrete.

3.3 Accelerated curing test

The main purpose of the proposed method was to inhibit ASR expansion by inhibiting expansion of alkali-silica gel. In order to quantitatively inspect the ASR expansion inhibitory effect resulting from applying the proposed method, accelerated curing tests were performed using concrete core material (Ø100×250 mm) extracted from retaining wall B before and after administering pressurized injections of lithium nitrite. The pre-injection core material was extracted 14 days before injection, and post-injection core material was extracted 7 days after completion of the ASR-Lithium

Method. The location of extraction for core material was selected at 250 mm from the injection holes. The accelerated curing test was performed under two exposure conditions of 40 °C at 95% relative humidity and 80 °C, both in a 1 N NaOH solution.

The measurements from the 40 °C and 95% relative humidity condition were based on "Measurement method for expansion rate using core sample material from concrete structures for which an alkali-aggregate reaction occurred (proposal)" of JCI-DD2[9]. After measuring the base length of the core, standard curing for approximately 2 weeks at 20 °C and 95% relative humidity was performed. The expansion strain within that time period was measured, and set as the open expansion ratio. After this, accelerated curing for 13 weeks at 40 °C and 95% relative humidity was performed. The expansion strain within that time period was measured, and set as the residual expansion ratio.

The measurements of cores stored at 80 °C in a 1 N NaOH solution were based on CSA A23.3-25A[10] and ASTM C 1260[11]. The core samples were initially maintained in hot water of 80 °C for 24 hours. The base length was measured followed by curing at 80 °C in a 1 N NaOH solution, and the expansion strain was measured 28 days after immersion. In both cases, measurement of expansion strain was conducted by attaching a stainless steel band with a gauge plug affixed to the core and measuring via a contact gauge.

4 RESULTS

4.1 Results of quantitative analysis of lithium-ion

The results of the quantitative analysis of lithium-ion for retaining wall A are shown in Figure 6. Based on the results of previous research, setting the minimum Li^+/Na^+ mole ratio required for the inhibition of ASR using lithium nitrite to 0.5 sugsests that the amount of lithium-ion required for ASR inhibition measures in this retaining wall is 0.459 kg/m^3. Alhough the concentration of injected lithium was 1.0 in Li/Na molar ratio, it was expected that concentration of lithium ion of within the concrete would vary greatly. The quantity of lithium ion found in low concentration areas was compared with necessary lithium quantity reported in the literature (Li/Na molar ratio is 0.5) [8]. As a result, the necessary lithium ion concentration to control ASR expansion in both retaining walls was 0.459 kg/m3 on the assumption that the minimum Li/Na molar ratio necessary for controlling ASR expansion as 0.5. While 3 out of a total of 24 samples were found to be slightly under 0.459 kg/m^3, the amount of lithium-ion was found to be above the required amount for 88% of the material tested. Also, the mean value of lithium-ion content for all 24 samples was 0.715 kg/m^3. This significantly exceeds the required amount of lithium-ion of 0.459kg/m^3.

4.2 Results of the accelerated curing test

The results of the accelerated curing at 40 °C and 95% relative humidity for core material extracted from retaining wall B are shown in Figure 7. The total expansion 3 months after accelerated curing of the core extracted before the injection of lithium nitrite was 0.081%. In contrast to this, the total expansion of the core extracted after injection was 0.018%. This is a 22.2% decrease compared to the pre-injection value. Compared via the residual expansion ratio, the pre-injection value is 0.052% and the post-injection was value 0.014%. This shows there was a decrease of up to 26.9% after administration of the proposed method.

The results of the accelerated curing at 80 °C in a 1 N NaOH solution are shown in the same manner in Figure 8. The expansion of cores extracted before the injection of lithium nitrite at 28 days of accelerated curing in this regime was 0.256%. In contrast to this, the expansion of a core extracted after injection was 0.110%. This indicates that there was a decrease in expansion by up to 43.0% compared to the pre-injection value.

5 DISCUSSION

5.1 Distribution of lithium-ion

The relationship between the distribution of lithium-ion and locations of the injection holes in retaining wall A is shown in Figure 11. Because it was thought that lithium-ion would permeate outward from the surrounding area from each injection hole, it was assumed that the concentration of lithium-ion would be the highest in the vicinity close to each injection hole and the concentration would decrease in a gradient farther away from the injection holes. However, the actual distribution revealed a high concentration of lithium-ion detected in the vicinity of the center area between the injection holes to the top and bottom (sample material No. 9 – 16). Looking at the relationship between the unevenness in distribution of lithium-ion compared to injection hole location, as indicated in Figure 12, lithium-ion permeating the vicinity of sample material No. 9 – 16 from the injection holes to the top, bottom, left, and right sides may be considered the cause of a high distribution of lithium-ion amount in the observed area. Also, regarding the permeation path when lithium-ion is administered via pressurized injection, the transfer of lithium-ion is not only along a pressure gradient or concentration gradient within the concrete matrix, but also affected significantly by flow through minute cracks within the concrete. Due to this, depending on the state of cracks within the concrete interior, the concentration of lithium-ion is not necessarily always higher in the proximity of the injection holes.

The distribution pattern of lithium-ion appears erratic. However, the concentration range of these test results, indicated that if pressure injection of aqueous solution of lithium nitrite was conducted with the injection hole interval set at 500 mm and the injection pressure set at 0.5 – 0.6 MPa for concrete with a compressive strength of 10.9 – 18.3 N/mm^2, lithium-ion is supplied above the amount required for ASR inhibition for a range of approximately 88% of the concrete interior.

5.2 Reduction of ASR expansion

The results of the accelerated curing test conducted at 40 °C and 95% relative humidity, the Ministry of Land, Infrastructure and Transport has designated as harmful or potentially harmful materials which exhibit an expansion amount of 0.05% or greater when cured for 13 weeks [6]. The expansion rate of the pre-injection core after 13 weeks significantly exceeds this threshold at 0.081%, and it can be determined that the possibility was high for expansion progressing in the concrete before receiving an injection of lithium nitrite. In contrast to this, the expansion rate of the post-injection core after 13 weeks was under this threshold at 0.018%, the indication being that the possibility was reduced for expansion progressing in the concrete after receiving an injection of lithium nitrite.

Because 3 months are required to obtain results of the accelerated curing test conducted at 40 °C and 95% relative humidity, it would be difficult to obtain confirmation results of effectiveness within the execution period for general repair works. Therefore, the focus was on the results of the accelerated curing test conducted at 80 °C in a 1 N NaOH solution, which produced results in a shorter time span. For this accelerated curing test, Katayama, et al. have stipulated that the expansion was under 0.10% for sound structures, including Japanese volcanic rock, at a period of 21 days [12]. If this value is assumed as the threshold for the accelerated curing test used herein, then the expansion rate of pre-injection core significantly exceeds this threshold at 0.215% after 21 days and the post-core expansion rate was below the threshold at 0.091% after 21 days.

The inhibitory effect of the ASR-Lithium Method was verified in both accelerated environments, by comparing the expansion of the core before and after injection. Also, differentials of pre- and post-injection expansion values indicated herein, further elucidated the inhibitory effect of ASR expansion resultant from the pressurized injection of lithium nitrite.

6 CONCLUSIONS

(1) This study showed that for the case in which a pressurized injection of lithium nitrite was administered into the interior of concrete structures through injection holes and injection pressure as stipulated by the proposed method, lithium-ion at a quantity above the amount required for ASR inhibition was supplied to a range of approximately 88% of the concrete interior.

(2) After pressurized injection in a concrete structure of a quantity of aqueous solution of lithium nitrate for which the Li^+/Na^+ mole ratio is 1.0, as per the results of an accelerated curing test performed on the core extracted from the said concrete at 40 °C and 95% relative humidity, we confirmed that the post-injection expansion rate was reduced as much as 22% below the pre-injection rate.

(3) Due to the result of favorable permeation of lithium nitrite and expansion rate reduction, it was concluded that the inhibitory effect of ASR expansion can be sufficiently expected through the proposed ASR-Lithium Method.

7 REFERENCES

[1] Japanese Society of Civil Engineers: Standard Specifications for Concrete Structures-2002. Materials and Construction, 2002

[2] Japanese Society of Civil Engineers: Concrete Library 124, Alkali Aggregate Countermeasure Subcommittee Report, 2005

[3] Inoue, H, Matsuzato, H, and Ayada, T (1995): Studies on corrosion protection method of reinforced concrete by applying inhibitor Part 2: Experimental study on the permeability of inhibitor into concrete. Japan Society For Finishing Technology, 1995 Annual Meeting: 19-22.

[4] Era, K, Okada, S, Mihara, T, and Kawahara, K (2004): Control of the alkali-aggregate reaction

by lithium nitrite power injection. Proceedings of the Concrete Structure Scenariis. Journal of the Society of Materials Science, Japan (4): 17-122.

[5] Era, K, Okada, S, Mihara,T, and Kawahara, K (2005): Verification of controlling effect of the alkali-aggregate reaction by lithium nitrite power injection. Proceedings of the Concrete Structure Scenariis. Journal of the Society of Materials Science, Japan (5): 189-194.

[6] Ministry of Construction (1988): Comprehensive technology development project, development of technology for the improvement of concrete durability. Report.

[7] Tremblay, C, Bérubé, MA, Fournier, B, and Thomas, MDA (2006): Effectiveness of lithium-based products in concrete made with Canadian aggregates susceptible to ASR. In: Fournier, B (editor): Marc-André Bérubé Symposium on alkali-aggregate reactivity in concrete. 8^{th} CANMET/ACI International Conference on Recent Advances in Concrete Technology, May 31 - June 3, 2006, Montréal, Canada: 217-240.

[8] Saito, M, Kitagawa, A, and Hasaba, S (1992): Effectiveness of lithium nitrite in suppressing alkali-aggregate expansion. Journal of the Society of Materials Science, Japan (41): 1375-1381.

[9] JCI-DD2 (1989): Determination of expansion rate of AAR-damaged structure using concrete core. Japan Concrete Institute: 4-8.

[10] CSA A23.3-25A (1994): Test method for detection of alkali-silica reactive aggregate by accelerated expansion of mortar bars. Canadian Standards Association, Mississauga, ON/CA: 236-242.

[11] ASTM C 1260 (1994): Standard test method for potential alkali reactivity of aggregates (mortar-bar method). Annual Book of ASTM Standards (04.02). American Society for Testing and Materials, West Conshoshocken, PA: 654-659.

[12] Katayama, T, Tagami, M, Sarai, Y, Izumi, S, and Hira, T (2004): Alkali-aggregate reaction under the influence of deicing salts in the Hokuriku district, Japan. Materials Characterization (53/2-4), Special Issue (29): 105-122.

Table 1: Process Specifications

Item	Unit	Wall A	Wall B
Core test results			
Total amount of alkali	kg/m^3	4.1	5.5
Compressive strength	N/mm^2	18.3	20.9
Tensile strength (estimate)	N/mm^2	1.83	2.09
	⇩		
Injection specifications			
Required amount of lithium nitrite	kg/m^3	17.5	23.5
Injection pressure range	MPa	0.5～0.6	0.5～0.7
Time required for injection	Hours	40	55

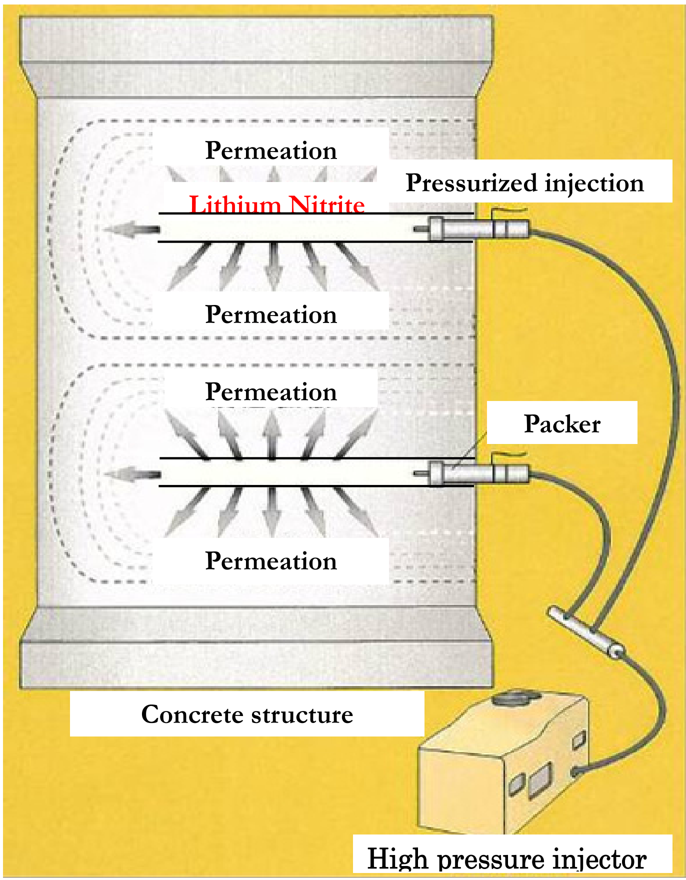

Figure 1: Process overview

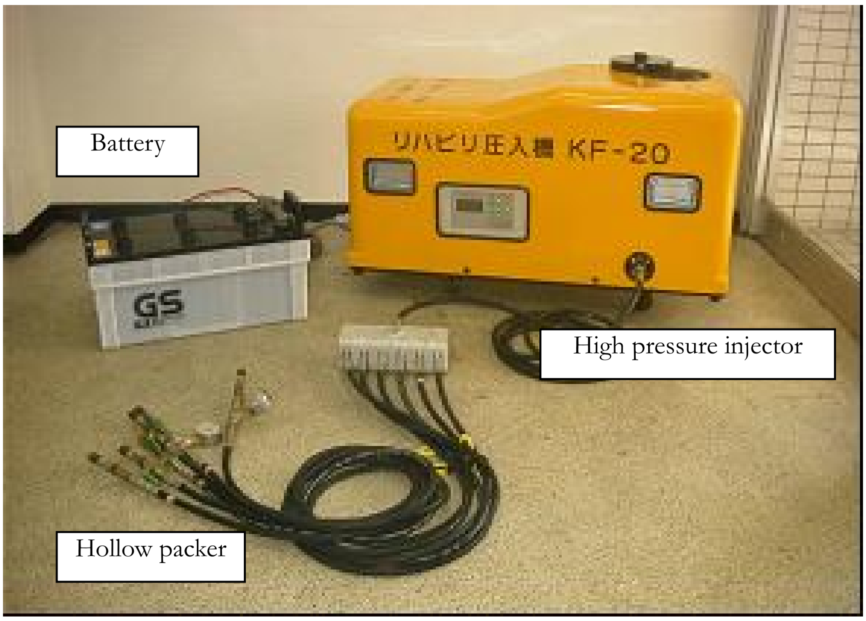

Figure 2: Equipment

Figure 3: Retaining wall A (injection)

Figure 4: Retaining wall B (before injection)

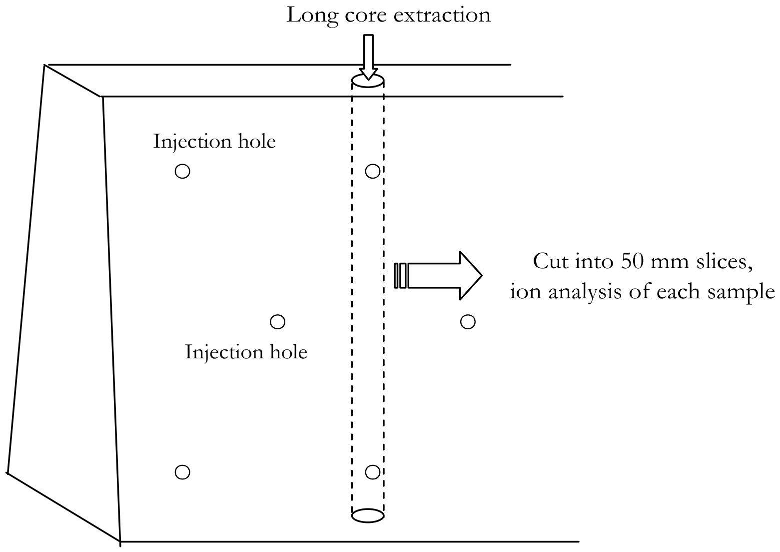

Figure 5: Extraction of lithium-ion analysis sample material

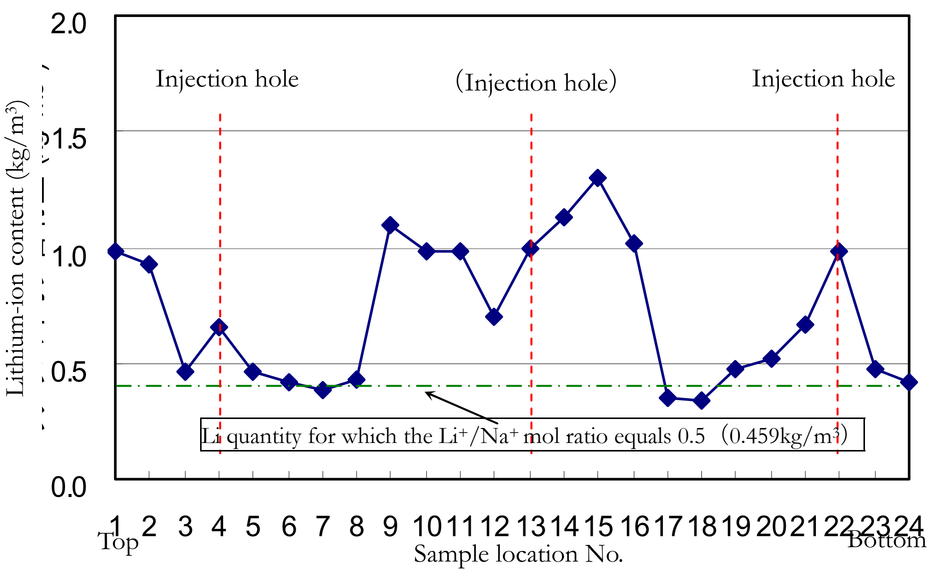

Figure 6: Lithium-ion is supplied over the amount required for ASR inhibition for a range of approximately 88% of the concrete interior.

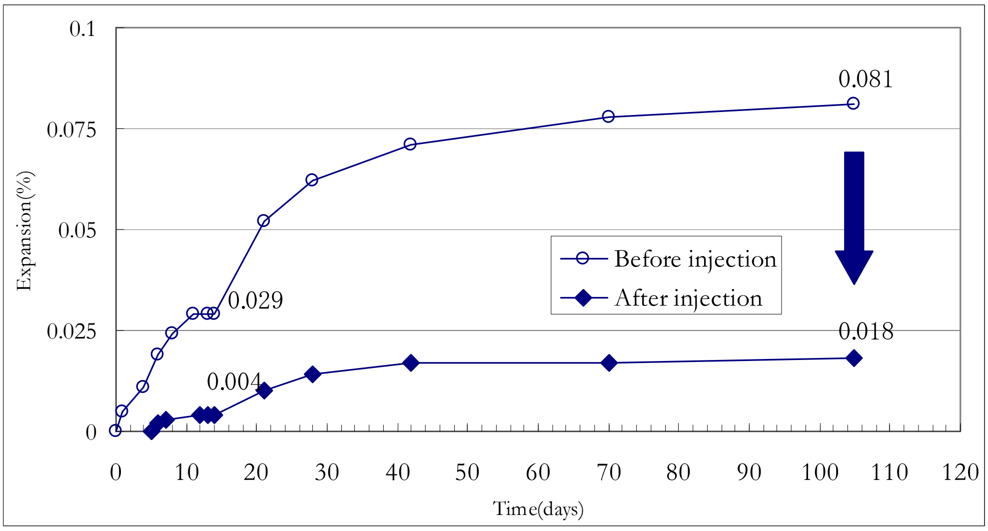

Figure 7: Results of the accelerated curing test at 40 degrees Celsius, RH 95%

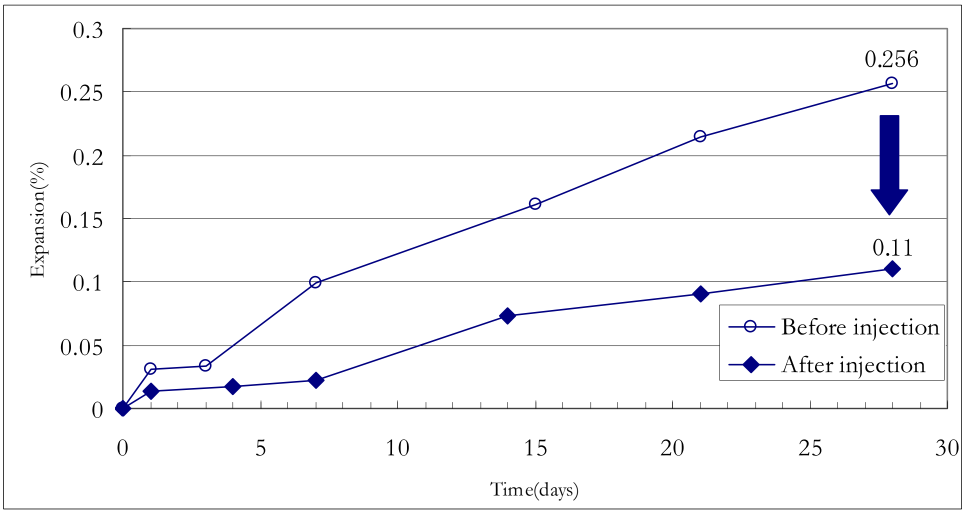

Figure 8: Results of the accelerated curing test at 80 degrees Celsius in a 1N NaOH solution

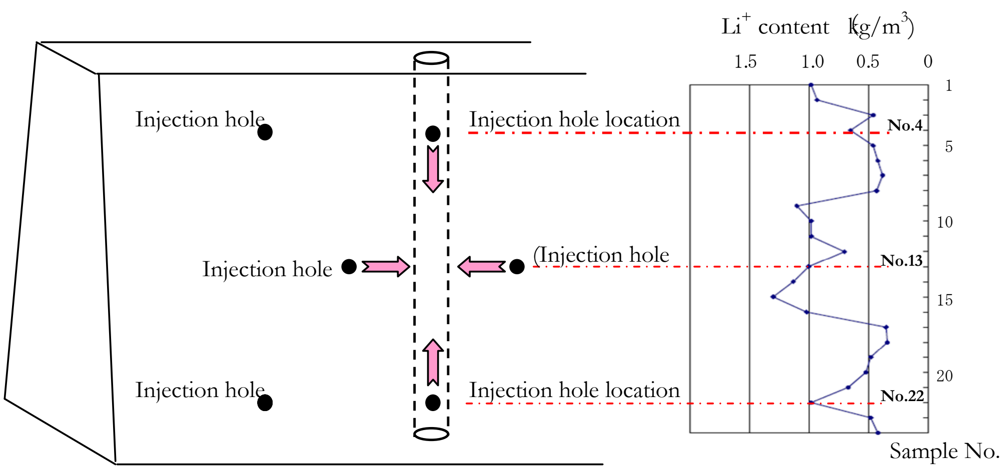

Figure 9: Relationship between extraction location of sample material and lithium-ion distribution