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Distribution of Lithium Nitrite Injected into Concrete and Its ASR Suppression Effect

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ABSTRACT

In this research, lithium nitrite was injected into ASR-deteriorated concrete specimens made with reactive aggregates in order to suppress further deterioration. The amount of injected lithium nitrite was set to three different levels, and the subsequent expansion behavior and area of lithium permeation were investigated. The area of permeation was checked using the coloring reagent TDI. It was found that the prescribed amount of lithium cannot be injected fully into the non-deteriorated specimens. When the lithium was injected at an early stage of deterioration, the area of permeation was small and the ASR suppression effect was small regardless of the injection amount. Also, the expansion reduction effect was evident when the lithium was injected into the considerably cracked concrete.

Keywords: ASR, lithium nitrite injection, repair, color reaction test.

1.0 INTRODUCTION

In recent years degradation of concrete structures due to alkali silica reaction (hereafter, ASR) has become a big issue. In structures where large cracks have been generated as a result of the excessive expansion due to ASR, not only the strength of the concrete is reduced, but also the reinforcement might occasionally rupture around the parts where the reinforcement has been bent or pressure welded. It is also known that when ASR occurs, resistances to frost damage and chemical attack deteriorate, and the performance for protecting rebars within the concrete from corrosion deteriorates. Frequently a surface coating is applied as a method of repair to prevent expansion by cutting off the supply of water from the outside, which is one of the factors causing the ASR degradation. However, if it is difficult to completely cut off the supply of water, so degradation may occur again after repair.

Under these circumstances, it has been proposed to apply lithium compounds for controlling ASR deterioration (McCoy 1951). While there are discussions on the mechanism how the lithium compounds works in mitigating ASR (Wijnen, 1989, Chatterji, 1987, Sakaguchi, 1982, Prezzi, 1997), the application of lithium compounds has been considered to be an effective method to prevent or mitigate ASR reaction, and has already been utilized for new construction by mixing them into concrete and for existing structures by spraying them on the structures' surface (FHA, 2006).

In recent years there has been an interest in the method of repair by injecting lithium nitrite into the concrete (Era, 2008). This is a method of reducing the expansion due to ASR by injecting lithium nitrite under pressure into the concrete of a structure which suffers ASR. Repair by lithium injection is frequently carried out when ASR has progressed to a certain extent, that is, the amount of expansion is about 1500 to 2000$\mu\varepsilon$. Nevertheless, it is desirable to carry out repair at an early stage of deterioration before the ASR becomes significant and the crack widths becomes large, from the point of view of reducing frost attack and chemical attack as well as chloride attack. However there is little knowledge regarding lithium injection at an early stage of ASR, and there are many unknown aspects.

In this research, injection of lithium nitrite into ASR test specimens prepared using reactive aggregates was carried out at three different ages and with three different lithium injection amount. A comparative analysis was carried out among the ages of injection at; (i) the stage without cracks, (ii) the stage where cracks could barely be found visually (about 400$\mu\varepsilon$ of expansion), and (iii) the stage at which injection repair is normally applied (about 2000$\mu\varepsilon$ of expansion). Also, coloring tests were carried out using the reagent toluene diisocyanate (TDI) to determine the area of lithium permeation.

2.0 OVERVIEW OF THE TESTS

2.1 Materials and mixtures

The test specimens were produced using reactive aggregates, ordinary Portland cement as the cement, and a water cement ratio of 57%. Also, sodium chloride was added to the concrete so that the equivalent alkali quantity was 9.0kg/m^3.

The lithium compound used as ASR suppression agent was lithium nitrite ($LiNO_2$), which is used most frequently in Japan. It was used as a 40% aqueous solution, the highest concentration that does not adversely affect the permeability into concrete (Era, 2008).

2.2 Test specimens

Figure 1 shows the dimensions of the test specimens and the positions of the drilled holes for lithium injection, and Table 1 shows a list of the test specimens. Lithium was injected at three different ages, and the test specimens were referred to as “undegraded injection specimens” into which lithium was injected prior to crack generations, “early injection specimens” into which lithium was injected when cracks could barely be visually determined with about 400$\mu\varepsilon$ of expansion, and “normal injection specimens” into which lithium was injected at about 2000$\mu\varepsilon$ expansion, which is when repair by lithium injection is normally applied. Undegraded injection specimens were prepared only for being investigated their lithium penetration areas.

Three levels of Li/Na molar ratios of 0.4, 0.6, and 0.8 were given to the specimens, and in addition “uninjected specimens” were prepared in which lithium injection was not applied. Test specimens were removed from their molds the day after concrete casting, cured for seven days wrapped by a wet cloth, then placed in a degradation acceleration chamber (temperature 35 to 40°C, humidity 100%), to start accelerated ASR degradation.

Table 1. List of prepared specimens

[Li/Na]	Undegradated injection	Early injection	Normal injection
Uninjected	—	A	A
0.4	A	A & B	A
0.6	A	A & B	A
0.8	A	A	A

A: A specimen, B: B specimen (see Fig. 1)

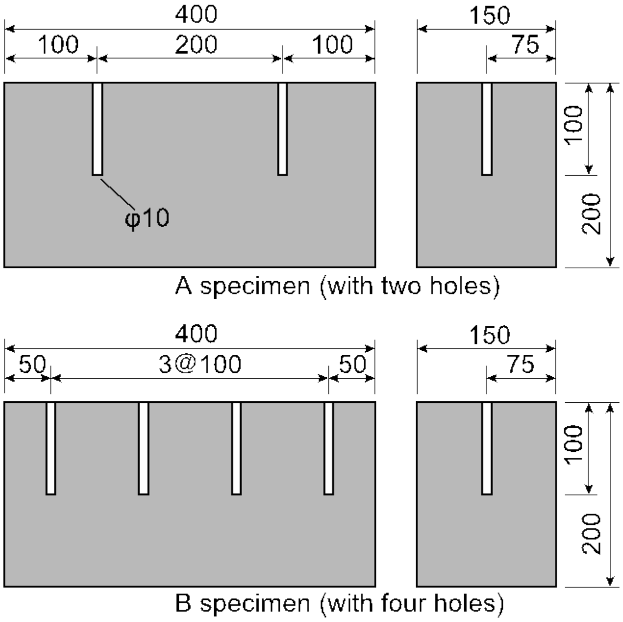


Fig. 1. Test specimens (unit: mm)

Also, two types of early injection specimens were prepared, test specimens A and test specimens B, with different positions and numbers of drilled holes but with the same amount of lithium injected, to investigate whether the suppression effect is increased by increasing the number of holes. However, test specimens A only were produced for normal injection specimens.

2.3 Measurement of expansion

Figure 2 shows the plug positions for measuring the expansion. Eight plugs were embedded into one side surface of the test specimens. There was a total of 10 measurement sections, each with a gauge length of 100 mm: four in the vertical direction (sections 1 to 4), three on the upper side in the horizontal direction (sections 5 to 7), and three on the lower side in the horizontal direction (sections 8 to 10), at which the change in length was measured every week.

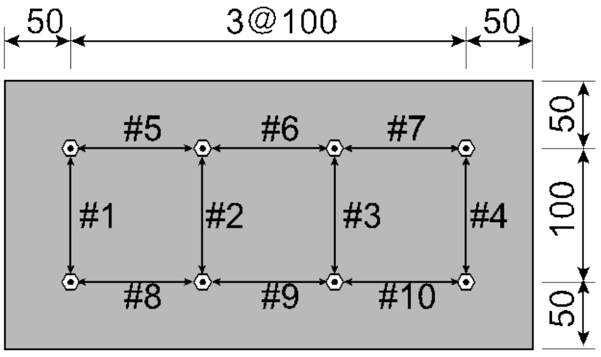


Fig. 2. Arrangement of plugs for measuring expansion (unit: mm)

2.4 Lithium injection

Lithium was injected on the early injection specimens when the expansion was about 400με, at which time cracks could be determined visually, and on the normal injection specimens when the expansion was around 2000με, as can be seen in Fig. 3.

In order to prevent leakage of the injected lithium from the cracks in the normal injection specimens, all the surfaces except the top surface of specimens were provided with a coating of polymer cement mortar of about 2 mm thickness. Note that this polymer cement was removed after the lithium injection was completed. This was to enable us to determine the expansion reduction effect due to lithium injection alone, as the polymer cement coating might suppress the further progress of ASR by blocking the ingress of water into concrete. Next, ϕ10×100 mm injection holes for injecting lithium were provided using a concrete drill, at two locations in each test specimen A and at four locations in each test specimen B. Fig. 1 shows the positions of the drilled holes in the specimens. In the case of the uninjected test specimens, even though lithium injection was not carried out, holes were drilled in order to investigate the expansion under the same conditions as the injection specimens. The injection pressure was 0.4 MPa for the undegraded injection specimens and the early injection specimens, and 0.2 MPa for the normal injection specimens, taking into consideration lithium leakage from cracks on the top surface of the test specimens. The amount of injected lithium nitrite was such that the molar ratios of Li/Na in the concrete were 0.4, 0.6, and 0.8. Note that it was confirmed in advance that expansion is not produced when the Li/Na molar ratio is as low as 0.4, when the lithium nitrite is added during mixing of the concrete.

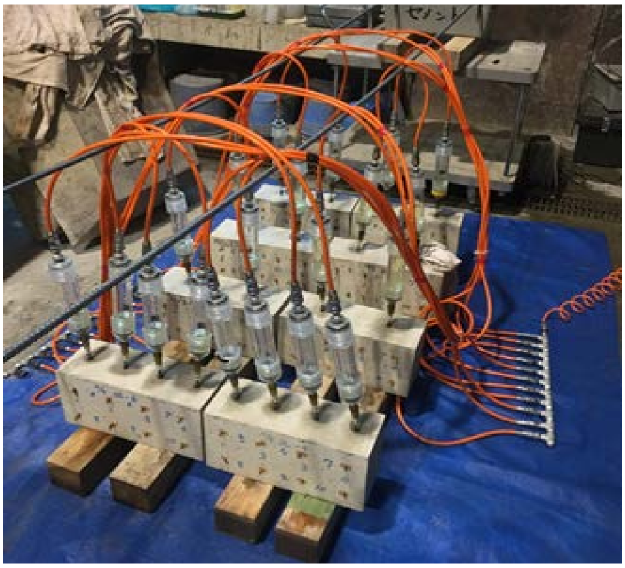


Fig. 3. Lithium nitrite injection

For all of the undegraded injection specimens, only about 50 mL of prescribed quantity was able to be injected into a single hole. The designed quantity of lithium could be completely injected into the early injection specimens within two weeks and into the normal injection specimens within one week.

2.5 Coloring tests

The test specimens were cut into 400×200×75 mm along the injection holes using a concrete cutter, and the color reaction reagent toluene diisocyanate (TDI) was sprayed onto the cut surfaces. TDI has the property that it reacts with the nitrite ions in the lithium nitrite to produce a brownish-red change of color, so the area over which the color changes can be regarded as the area of permeation of the nitrite ion. It is the lithium ion that exhibits the ASR reduction effect, so actually the target of detection should be the lithium ion and not the nitrite ion. However, the nitrite ion and the lithium ion transfers substantially together through the concrete as a result of injection of the aqueous solution of the lithium nitrite, so the colored area can also be cosidered to indicate the distribution of the lithium ion (Era, 2005).

3.0 RESULTS & DISCUSSIONS

3.1 Expansion suppression

The variation of the vertical expansion, which is the average of expansions measured at #1, #2, #3, and #4, with time after injection of lithium nitrite is shown in Fig. 4 for the early injection specimens, and in Fig. 5 for the normal injection specimens.

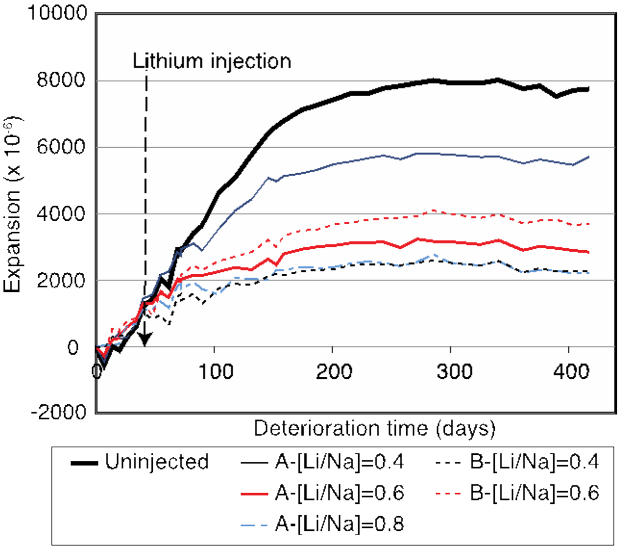


Fig. 4. Expansion of early injection specimens

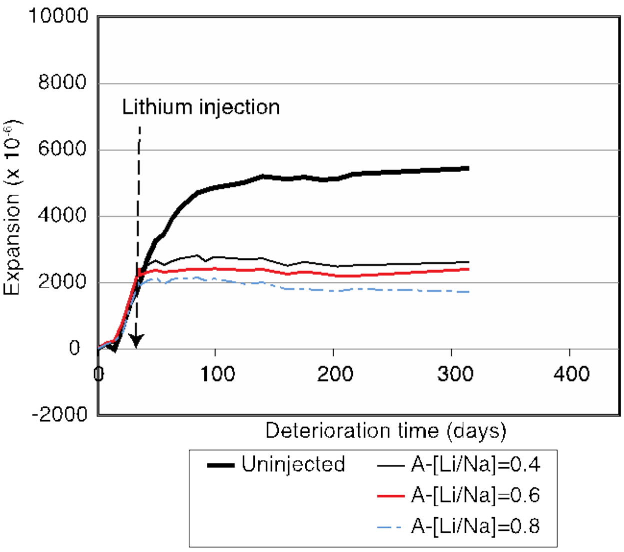


Fig. 5. Expansion of normal injection specimens

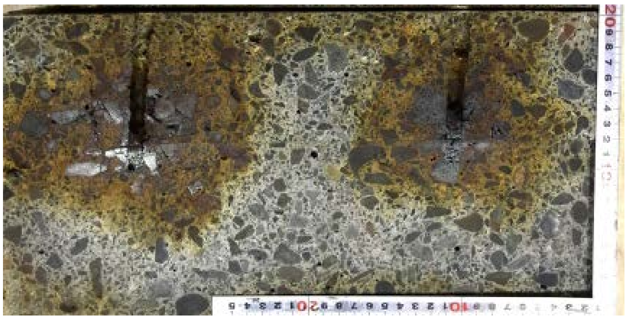
From Fig. 4, it can be seen in early lithium injection specimens that the expansion are smaller than in uninjected specimens. However, expansion is not completely suppressed immediately after the injection. For the specimens A with Li/Na ratio of 0.4, which showed the smallest area of lithium permeation, the expansion was about 2/3 of that of the uninjected specimens, and for the other specimens with larger Li/Na ratio, the expansion was about 1/3. Also, for the 0.8 molar ratio test specimen, the rate of expansion slowed down and the expansion tended to converge at around 2000με. With specimens B that were provided with an additional injection hole, the expansion was reduced compared with the uninjected test specimen and was about the same as that for test specimens A with molar ratios 0.6 and 0.8.

Next, Fig. 5 shows the results for the normal injection specimens into which the lithium was injected when the was about 2000με. In contrast to the early injection specimens, the expansion suppression effect can be seen immediately after the lithium injection even if the Li/Na ratio was 0.4, and the expansion suppression effect of lithium injection can be seen in all test specimens.

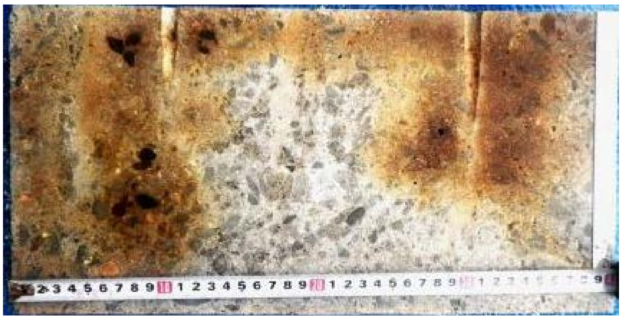
3.2 Coloring tests

Figure 6 shows photographs after the coloring tests. The area with a brownish-red color change corresponds to the nitrite permeation area, which in this research is regarded to be equivalent to the lithium permeation area. Near the injection holes, the color change is dark, but it becomes lighter with distance from the injection holes. It is reported that the expansion suppression effect is exhibited in the concrete with the color change (Era, 2005). Also, it is considered that the transfer of lithium nitrite by diffusion after being injected into concrete is smaller than that by pressurized injection. Therefore here it is assumed that the area where nitrite ion and lithium ion are present did not change after the injection until the coloring tests were carried out.

Undegradated injection-A-[Li/Na]=0.6



Early injection-A-[Li/Na]=0.6



Normal injection-A-[Li/Na]=0.6

Fig. 6. Examples of coloring test

Table 2 shows the colored area in each specimen. As stated previously, it was not possible to inject all the prescribed quantity of lithium into the undegraded injection specimens, so the area of permeation was small compared with the other specimens. It is considered that this was because there were no microcracks due to ASR in the concrete, so there was no lithium permeation through these cracks.

Next, in the specimens A of the early injection specimens, the permeation area was somewhat larger the greater the injected lithium amount, but the differences of the area among them were small. The permeation area was a maximum of about 50%, so it is considered that the lithium was not spread appropriately throughout the whole test specimen. On the other hand, in the test specimens B in which the number of holes was increased, the permeation area was about 70%. However, in all the specimens it tended to be difficult for the lithium to permeate to the bottom of the test specimen, which was far from the injection holes.

Table 2. Results of coloring test

	[Li/Na]	Type	Vertical Expansion ($\mu\varepsilon$)	Colored area (%)
Undegra-dated injection	0.4	A	--	18.8
	0.6		--	24.6
	0.8		--	30.0
Early injection	0.4	A	5713	44.3
	0.6		2840	48.1
	0.8		2220	49.2
	0.4	B	2270	72.6
	0.6		3698	68.5
Normal injection	0.4	A	2613	74.0
	0.6		2403	71.9
	0.8		1725	87.3

With the normal injection specimens, while the lithium did not spread throughout the whole test specimen, the permeation area was larger than for the early injection specimens, even though the injection pressure was only 1/2 of that of the other test specimens. For example, the permeation area achieved with the 0.8 Li/Na ratio specimen with only two holes was about the same as that for the early injection test specimens with four holes.

From the above, it can be seen that the effect of the degree of ASR degradation of the concrete on the efficiency of injection is large. It is considered that this is because the microstructure of the concrete has been loosened by the ASR, and is mainly due to differences in the degree of crack propagation. In other words, the lithium ion is transferred by the pressure gradient, but it mainly moves through the cracks in priority, and from there penetrates into the matrix.

3.3 Comparison of expansion and lithium permeation area

In the early injection specimens, expansion suppression effect was small. Expansion continued at least for 100 days after the accelerated degradation being re-started and thereafter expansion became slower. Especially, the expansion in the specimens A with 0.4 Li/Na ratio was larger than the other early injection A specimens. However, the permeation area of this specimen was similar to those of the other early injection A specimens. Also, it was found that while there was a large difference in permeation areas between the specimen A series and the specimen B series, a difference in the expansion suppression effect was small except for the 0.4 Li/Na ratio specimen.

On the other hand, while all the normal injection specimens were specimens A with only two injection holes, the amount of injected lithium was sufficient to virtually stop expansion immediately after injection and prevent further degradation due to ASR, even for the 0.4 Li/Na ratio specimen in which the injected amount was the smallest. Given that the permeation area of lithium shown in Table 2 is large, it is considered that the progress of ASR was suppressed by the penetration of lithium throughout the majority of the area of the test specimens.

For the early injection specimens, lithium was injected at the stage where there was no significant cracking on the surface of the concrete, with the aim of suppressing the progress of ASR at an early stage. However considerable time was required to complete injection in the case of early injection, and in addition expansion did not immediately stop. Also, by observing the trend in expansion after completion of injection, it was found that the amount of expansion was either unchanged from or greater than that of normal injection test specimens with the same number of injection holes. Therefore early injection was not effective in suppressing ASR, and on the contrary it is more effective to carry out lithium injection after cracks have developed to a certain extent.

In addition, there are various theories regarding the mechanism of suppression of ASR by lithium ion, and the lithium may affect the deterioration suppression in various ways depending on the stage of ASR progress at which the lithium is committed, and may also affect the subsequent expansion. Therefore, it is necessary to investigate in detail the mechanism of ASR suppression by lithium in the future.

4.0 CONCLUSIONS

In this research lithium nitrite was injected into test specimens made with reactive aggregates. The lithium was injected at 3 different stages, undegraded, early (expansion of 400$\mu\varepsilon$), and normal (expansion of 2000$\mu\varepsilon$), the injected lithium amount was set to be Li/Na molar ratios of 0.4, 0.6, and 0.8, and the subsequent expansion behavior and area of lithium permeation were investigated. The area of permeation was estimated using the color change reagent TDI. It was found that when injection was carried out on the concrete without deterioration, the prescribed amount of lithium could not be injected fully. When lithium was injected at early stage of ASR deterioration, the area of permeation was small and the ASR suppression effect was small regardless of the injected lithium amount. Also, when lithium was injected after cracks had extended, the expansion suppression effect was considerable.

The conclusions obtained in this research were as follows:

1) Expansion

Expansion was reduced with the early injection test specimens, but it was not possible to completely suppress expansion immediately after injection even when the injected lithium amount and the number of injection holes were increased.

With the normal injection specimens, lithium injection could suppress the expansion, even with an Li/Na molar ratio of 0.4.

2) Coloring tests

It was hard to permeate lithium into the specimens without degradation by ASR, and also hard for the early injection test specimens to achieve appropriate injection.

With the normal injection specimens, the area of permeation was larger than for early injection, while the lithium did not permeate into each corner of the test specimen completely.

3) Comparison of expansion and permeation area

Unlike with the early injection specimens, the expansion suppression effect was obtained immediately after injection into the normal injection specimens.

The suppression effect may change depending on the stage of ASR progress.

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