CONTROLLING ASR EXPANSION BY LITHIUM ION PRESSURIZED INJECTION METHOD

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Abstract

Recently, lithium ion pressurized injection method has been spotlighted as the repair method of concrete structure which deteriorated by ASR. In this study, the effect of lithium ion on ASR expansion was investigated. The elemental analysis of the ASR gel specimen to which lithium ion had been supplied was also performed by using SEM, EPMA and TOF-SIMS. The change of the physical form of the ASR gel due to the supply of lithium ion was not found by SEM observation. However, the elemental analysis by TOF-SIMS enables to obtain the element mapping of the lithium ion in ASR gel. Furthermore, the elemental analysis by EPMA and TOF-SIMS demonstrated that lithium ion by the pressurized injection method has extended to the ASR gel. The compositional ratio of [Li] to [Na] in the ASR gel was able to be presumed.

Keywords: ASR, Lithium ion, SEM, EPMA, TOF-SIMS

1 INTRODUCTION

Lithium (Li) ion treatment is gathering attention as a means of repairing concrete structures that have become deteriorated as a result of alkali silica reactions (ASR) [1]. More specifically, the Li ion pressurized injection method, which quickly delivers Li to the interior of concrete structures, is being put into practice [2,3]. In this method, lithium nitrite ($LiNO_2$) is pressure-injected through a small hole cored into a concrete body in order to suppress subsequent expansion of the structure due to ASR. The proposed mechanism involves the non-expanding chemical transformation of alkali silica gel (hereinafter referred to as the "gel") caused by ion exchange between Na^+ in the gel and Li^+ [4]. However, since there have been only a limited number of studies on the distribution of Li ions in the gel, the details of this ion exchange mechanism are still unclear.

In the present study, the Li ion pressurized injection method was applied to specimens which had expanded by approximately 1,500 μstrains due to ASR, in order to evaluate the mitigating effects of Li ions. Gel samples were taken from each ASR specimen, and image mapping and quantitative analysis of the distribution of Li ions were carried out.

2 OUTLINE OF THE TEST

2.1 Specimens

The concrete mix for testing is given in Table 1. Pyroxene andesite from Hokkaido was used for both the coarse and fine reactive aggregates. This material is judged not to be harmless in JIS A 5308 "Alkali Silica Reactive Test (Chemical Method) on Aggregate". For the non-reactive aggregate, crushed stone from

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Tsuchiyama and river sand from the Yasu River were used. Based on the results of a pessimum test, the mix proportion of the reactive aggregate was determined to be 70% for the fine aggregate and 50% for the coarse aggregate. The amount of alkali to be introduced was set to 8 kg/m^3 Na_2O equivalent. The Li compound to be used as an ASR suppressor was a 40% $LiNO_2$ solution. The diameter of concrete specimen is 100mm and height is 200mm. A total of six contact chips, two on the top and four on the side, were attached to the specimen surface in order to measure the amount of expansion.

2.2 Materials and mixture proportions

As shown in Table 2, the test was performed with varying amounts of $LiNO_2$ and two different supply methods: (i) pre-mixing and (ii) pressure-injection. For the pre-mixed case, $LiNO_2$ equivalent to Li/Na mole ratios of 0.4, 0.8 and 1.2 was supplied at the time of concrete mixing. In the pressurized-injection case, the specimens were subjected to an expansion-promoting environment until the amount of ASR expansion exceeded 1,500 μstrains and cracks with a width of 0.2 to 0.4 mm were initiated. A 40% $LiNO_2$ solution, corresponding to Li/Na molar ratios of 0.4, 0.6 and 0.8, was then pressure injected. The ASR expansion-promoting environment was a chamber with a temperature of 40°C and a humidity of 95%. During the test, expansion strain was measured on a biweekly basis. Figure 1 is a photograph showing the pressurized injection method for Li ions.

2.3 Elemental analysis

A specimen not supplied with Li (hereafter referred to as the reference specimen) and one pressure-injected to a Li/Na mole ratio of 0.6 were split by a load. Regardless of the presence or absence of Li ions, both specimens exhibited a reaction rim at the perimeter of the aggregate particles and whitish gel deposits around the aggregates on the split surface. After observing the split surface, the gel was examined using scanning electron microscopy (SEM). A polished thin section of the Li-injected specimen was extracted from the location indicated in Fig. 2, a carbon coating was applied, and the distributions of Na, K, Si and Ca in the gel were analyzed using electron probe micro-analysis and energy-dispersive X-ray spectroscopy (EPMA/EDS, hereinafter referred to simply as "EPMA").

Generally, the elemental range for which EPMA is sensitive is from boron (B) to U (uranium), and hence is not capable of analyzing Li. For this reason, the specimen was irradiated with Ar (argon) and Ga (gallium) ion beams under ultra-high vacuum conditions in order to produce secondary ions. By measuring the flight time of these secondary ions, Li could be detected using time-of-flight secondary ion mass spectroscopy (TOF-SIMS), which can detect the constituent elements. Although in theory the resolution of TOF-SIMS is sufficient for analyzing Li, this method has almost never been applied to concrete-related studies. The polished thin section used for the EPMA analysis was also used for the TOF-SIMS analysis, but no carbon coating was applied because it inhibits the generation of secondary ions in TOF-SIMS.

The distributions of the constituent elements in the gel were color-mapped based on the qualitative EPMA and TOF-SIMS results. Quantitative EPMA and TOF-SIMS analyses were also performed to identify the chemical compositional ratio of each constituent element in the gel. These analyses were conducted 430 days after the specimens were placed in the expansion-promoting environment, which corresponds to 242 days after the pressurized injection method was implemented.

3 TEST RESULTS AND DISCUSSION

3.1 Results of promoted expansion tests

Figure 3 plots the amount of expansion of specimens. The reference specimen began to expand dramatically after 142 days in the chamber. On day 410, when the test was terminated, the amount of

expansion was about 5,800 μstrains. For the specimens pre-mixed with Li, no expansion was observed even after 410 days, which indicates the dramatic effect of Li ions in suppressing ASR expansion. No dependence was found on the amount of $LiNO_2$ added.

The $LiNO_2$ pressurized injection method was applied on day 188 when the amount of expansion had reached approximately 1,500 μstrains. The bore hole was filled with a non-shrink grouting material immediately after the completion of injection, and the specimens were placed back in the high-temperature chamber. Although all of the pressure-injected specimens exhibited a rapid expansion before $LiNO_2$ injection, no further expansion occurred up to 222 days after injection, regardless of the amount of $LiNO_2$ injected.

When pre-mixed, Li ions can be assumed to be uniformly distributed in the concrete. However, this would not be the case for pressurized injection because the movement of ions would depend on the presence of cracks, the crack widths and the density of the concrete. Thus, the supply efficiency is expected to be lower for pressurized injection so that a larger amount of $LiNO_2$ would be required. However, the results of the tests show that, for both methods, a Li ion mole ratio of 0.4 or more can suppress ASR expansion, which seems to suggest that there is no difference in the amount of Li ions needed. This is probably because the specimens used in the test were small and the pressurized injection procedure was strictly controlled in the laboratory. When pressurized injection is actually used in the field, it is expected that care might be needed in ensuring that the Li ion supply is sufficient throughout the structure. Further study is also needed for Li/Na mole ratios of less than 0.4.

3.2 Gel observation by the electron microscopy

Figures 4 and 5 show SEM images of gel observed on the split surface of the reference specimen and a pressure-injected specimen, respectively. Figures 4(a) and 4(b) show an amorphous alkali-silica type gel observed near an aggregate interface, whereas image 4(c) shows a crystallized alkali-calcium-silica type gel near the cement paste. These are known to be typical ASR products. Moreover, the gel near the aggregate interface, shown in Figs. 5(a) and 5(b), is also amorphous and an alkali-silica type, whereas the gel near the cement paste, shown in 5(c), is a crystallized alkali-calcium-silica type. A comparison of Figs. 4 and 5 indicates that the presence of Li ions caused no changes in the physical structure of the gel.

In a previous study, Mo, et al.[5] showed the results of SEM observations in which crystalline products formed around reactive aggregates in mortar with LiOH supplied, suggesting that a non-expanding substance, different from the normal gel, was formed as a result of supplying Li ions. While Mo et al. observed specimens prepared by supplying Li ions at the time of mortar mixing, in the present study, ASR-deteriorated concrete supplied with Li ions by pressurized injection was observed. Supposedly, when Li ions are pre-mixed into the concrete or mortar, gel is formed around aggregates, but before it expands due to water absorption, it reacts with Li and transforms into a non-expanding gel. On the other hand, when Li ions are pressure-injected, the gel formed in the concrete or mortar expands upon water absorption, after which the Li ions are injected. Consequently, with the pressurized injection method, no physical transformation of the gel already present in the concrete occurs.

3.3 Gel constituent element mapping

Based on the assumption that the mechanism by which Li ions suppress ASR expansion is the generation of a non-expanding gel, it might be expected that some change occurs to the gel immediately after the provision of Li ions. However, the SEM results revealed that there was no change in the physical form of the gel due to the presence of Li ions. Nevertheless, as shown in Fig. 3, the expansion was clearly controlled in the pressure-injected specimens. This leads to the premise that the Li ions infiltrate the gel or sol before

solidification and substitute for the alkali ions therein, so that the chemical composition changes to that of a non-expanding gel, although the physical form remains the same. To confirm this, a polished thin section of the specimen supplied with Li ions by pressurized injection to a Li/Na mole ratio of 0.6 was carbon-coated, and EPMA-based elemental mapping was performed for a qualitative analysis of the elements contained in the gel. Figure 6 presents an SEM image of a 500 μm×500 μm area and the associated element maps for Na, K, C, Si and Ca. The color scale on the right hand side of each map indicates the concentration of that particular element; the color on the top represents the highest concentration.

In the SEM image in Fig. 6, the dotted line represents the boundary between an area of fine aggregate (lower left) and cement paste (upper right). This is inferable from the distributions of Si and Ca. A crack that penetrates the cement paste and the fine aggregate is observed near the center of the image. In the element maps for Na, K and Si, the areas indicated by ovals contain high concentrations of these elements. Since alkali metals such as Na, K and Si are the main elements that constitute the gel, the gel is presumed to have formed on the fine aggregate surface and on both sides of the crack.

In order to determine the distribution of Li in the area shown in Fig. 6, a qualitative analysis on Li was performed using TOF-SIMS, and the resulting Li map is shown in Fig. 7. It can be seen that high concentrations of Li are found in the same regions where Na, K and Si exist in considerable quantities, as indicated by the oval regions in Fig. 7. This confirms that Li penetrates the gel formed around aggregate interfaces and cracks. However, as indicated by the dotted oval region in Fig. 7, a large amount of Li is also present in the cement paste near the aggregate. These results suggest that Li is transported not only along cracks, but also through interconnected pores in the concrete matrix. It can be assumed that only the Li present in the gel itself actually contributes to suppressing ASR expansion.

3.4 Quantitative analysis of Li ions in the gel

Figure 7 provides qualitative evidence that Li ions are present in the gel following pressurized injection. Assuming that the ASR control mechanism involves the formation of a non-expanding gel due to ion exchange between Na and Li, the abundance ratio of Na to Li that leads to this non-expanding gel can be used to determine the appropriate amount of Li ions that must be supplied by pressurized injection. To this end, elemental quantitative analyses using EPMA and TOF-SIMS were performed to ascertain the ratio of Na to Li in the gel at the positions shown in Fig. 8. Figure 8(a) shows the specimen injected with Li ions, where ◎1 to 3 are the positions for EPMA analysis and ◎4 and 5 are for TOF-SIMS analysis. Fig. 8(b) is an SEM image from the reference specimen, and ●1 to 3 are the positions for EPMA analysis.

Table 3 summarizes the relative content of different elements obtained in the analysis. For the specimen injected with Li ions, the gel formed inside the aggregate (1 and 2 in Fig. 8(a)) and outside the aggregate (3 in Fig. 8 (a)) were examined. However, there was no significant difference in the Si, Ca, Na and K content, which are the main constituent elements of the gel. For the Li-injected specimen, the Na content in the gel was 6.26% to 7.92% (6.82% on average), whereas in the reference specimen it was 7.39% to 8.81% (7.90% on average). The lower value for the Li-injected specimen is thought to be the result of substitution of Na in the gel by Li. It should also be pointed out that the analyzed gel samples were taken from different specimens and so the initial contents of Na could have been different.

As mentioned, EPMA cannot be used to detect Li. Furthermore, even with TOF-SIMS, it is difficult to directly quantify the elements contained in the specimens, because this technique is affected by the ionization efficiency of the secondary ions to be detected. Thus, in addition to the specimens analyzed by EPMA, a polished thin section of a standard specimen of spodumene, which contains Li and has known ratios of the constituent elements, was prepared and subjected to TOF-SIMS to map each element, thereby

deriving the number of dots present on the mapping image per element. The distributions of Li, Na, K, Si, Ca and all the other elements in the analyzed specimen detected by TOF-SIMS are given in Fig. 9. Table 4 shows the count for each element at positions ◎4 and 5 in Fig. 9 and in the standard specimen. The numbers represent relative ion intensities, calculated by normalizing the counts with the count for Si, which has the highest compositional ratio, being 100,000.

The Li ion content in the analyzed specimen was estimated by comparing the counts based on the elemental map with the theoretical values for the elements in the standard specimen to ascertain the correlation between the count for each element in the TOF-SIMS map and the actual elemental content. In the standard specimen, the known contents of Li_2O and SiO_2 are 8.03% and 64.58%, respectively. Using these values and the relative ion intensities of Li and Si in the gel and the reference specimen shown in Table 4, the content of Li_2O in the gel can be derived from Equation (1), and is calculated to be 0.64% inside the aggregate and 0.54% outside.

$$[Li_2O]=([Li_2O_{RT}]/[SiO_{2RT}])\times([Li_{CO}]/[Li_{RCO}])\times[SiO_2] \qquad (1)$$

Here, Li_2O is the amount of Li_2O (%) in the analyzed specimen, Li_2O_{RT} is the known amount of Li_2O in the standard specimen (%), SiO_{2RT} is the known amount of SiO_2 in the standard specimen (%), Li_{CO} is the Li count in the analyzed specimen, Li_{RCO} is the Li count in the standard specimen, and SiO_2 is the amount of SiO_2 in the analyzed specimen (%).

When the Li_2O content in the gel derived here is compared with the Na_2O content shown in Table 3 in terms of the mass ratio of oxides in the gel, the Li_2O to Na_2O ratio is 1/9.8 to 1/12.4 inside the aggregate and 1/12.5 outside. In terms of the Li/Na mole ratio, this represents a value of 0.17 to 0.21 inside the aggregate and 0.17 outside. In other words, from the injected Li/Na mole ratio of 0.6, the amount of Li that caused the gel to become non-expanding, corresponded to a Li/Na mole ratio of 0.17 to 0.21. It must be noted, however, that this result was simply obtained from the abundance ratio between Li and Na for the non-expanding gel. Even within the same specimen, this value may greatly vary depending on the position analyzed.

4 CONCLUSIONS

The following findings were obtained in the present study.

1) By pre-mixing Li ions in concrete with a reactive aggregate and a Li/Na mole ratio of 0.4, ASR expansion was found to be suppressed. Also, by adding Li ions into ASR-deteriorated concrete by pressurized injection to a Li/Na mole ratio of 0.4, ASR expansion after the injection was suppressed.
2) SEM observations of the gel formed after the Li ion pressurized injection revealed no change in the physical form of the gel due to the Li ions.
3) Although Li ions in the gel could not be detected using EPMA, it was shown to be feasible using TOF-SIMS, and elemental mapping was carried out.
4) Elemental mapping using EPMA and TOF-SIMS showed that Li ions introduced by pressurized injection are present in the gel. Also, the results of a quantitative elemental analysis indicated that the Li ion exists at a rate of the Li/Na molar ratio of 0.17 to 0.21 in gel.

5 REFERENCES

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Table 1: Mix proportion of concrete

W/C (%)	s/a (%)	Unit content (kg/m^3)					
		W	C	Sand		Gravel	
				Reactive	Non-reactive	Reactive	Non-reactive
63	45.7	183	290	574	239	493	495

Table 2: Specimen types of expansion test

Reactive Aggregate	Lithium nitrite ($LiNO_2$)		Number of specimens
	Supply method	Mol ratio (Li/Na)	
Andesite	No addition	—	3
	Premixture	0.4	3
		0.8	3
		1.2	3
	Pressurized injection	0.4	3
		0.6	3
		0.8	3

Table 3: Selected compositions of ASR gel in concrete by EPMA(EDS)

	The ratio of the elements contained in ASR gel (%)					
	ASR gel with Lithium ion			ASR gel without Lithium ion		
	1*	2*	3**	1*	2*	3*
SiO_2	56.72	56.74	59.64	56.07	59.43	53.18
TiO_2	0.74	1.03	0.30	0.05	0.02	0.63
Al_2O_3	0	0	0	0	0.64	0.06
Fe_2O_3	0	0	0.44	0.60	0.28	1.32
MnO	0.60	0.24	0	0.02	0	0.14
MgO	0	0	0	0	0	0
CaO	11.79	10.87	10.15	12.16	12.60	10.71
Na_2O	7.92	6.26	6.77	8.81	7.50	7.39
K_2O	1.83	1.91	1.64	1.63	1.02	1.97
SO_3	0.29	0	0	0	0	0.05
P_2O_5	0.77	0.34	0.78	0.90	0.71	1.04
Total	80.66	77.38	79.73	80.24	82.19	76.47
Li_2O***	0.64	0.64	0.54	-	-	-

* The ratio analyzed in the ASR gel inside aggregate

** The ratio analyzed in the ASR gel outside aggregate

*** The ratio analyzed in the ASR gel by TOF-SIMS

Table 4: Secondary ion relative intensity in ASR gel in concrete by TOF-SIMS

Ion classification		ASR gel in concrete		Reference rock
Kind	Atomic mass	4*	5**	spodumene
Li	7	31 831	25 389	348 713
Na	23	2 840 766	2 075 865	135 488
Mg	24	9 773	9 617	19 569
Al	27	24 053	23 391	336 146
Si***	28	100 000	100 000	100 000
K	39	121 181	109 129	82 675
Ca	40	14 240	11 545	136 146

* The number of counts analyzed in the ASR gel inside aggregate

** The number of counts analyzed in the ASR gel outside aggregate

*** The number of counts of Si normalized to 100 000

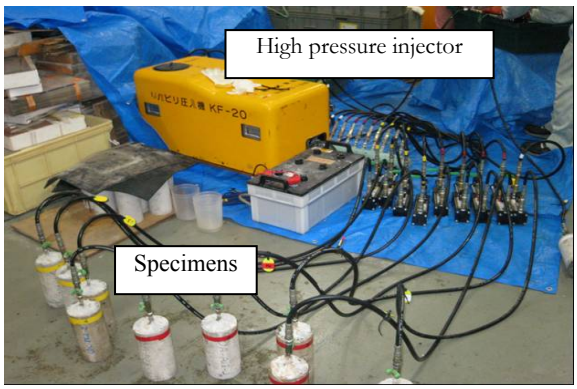

Figure 1: Equipments of pressurized injection

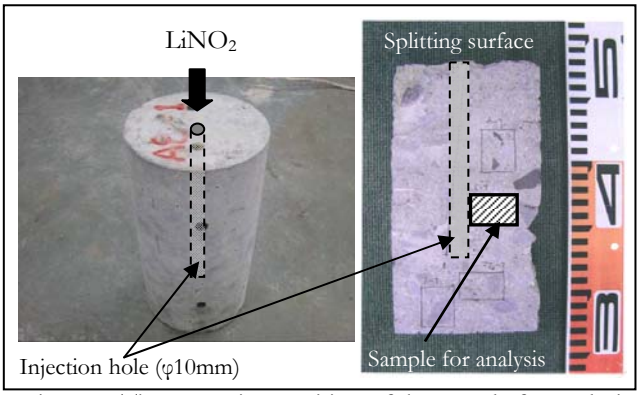

Figure 2: The extraction position of the sample for analysis

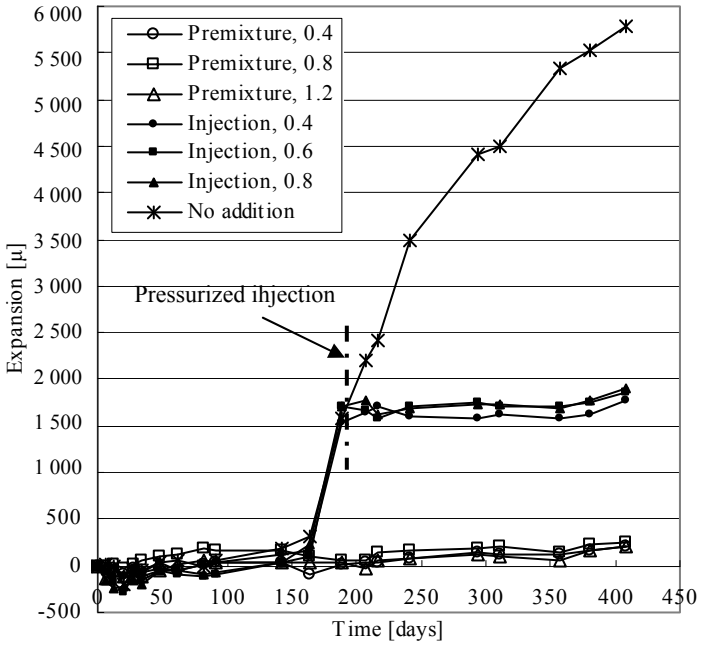

Figure 3: Expansion of concrete specimen

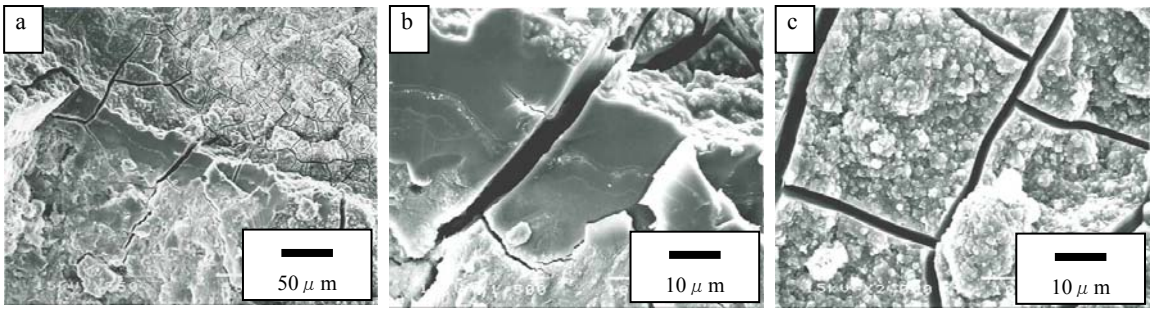

Figure 4: SEM micrographs of ASR gel without Lithium ion : (a)Amorphous gel near an aggregate interface, (b)The enlargement of amorphous gel near an aggregate interface, (c)Gel whose surface is crystallizing near cement paste

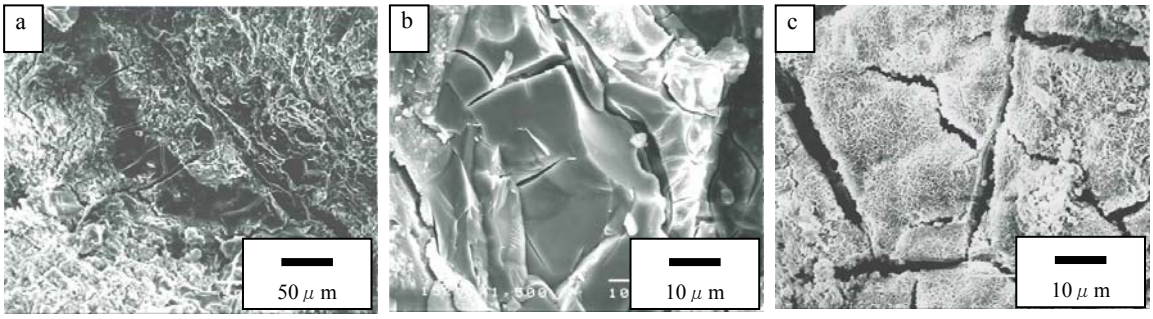

Figure 5: SEM micrographs of ASR gel with Lithium ion : (a)Amorphous gel near an aggregate interface, (b)The enlargement of amorphous gel near an aggregate interface, (c)Gel whose surface is crystallizing near cement paste

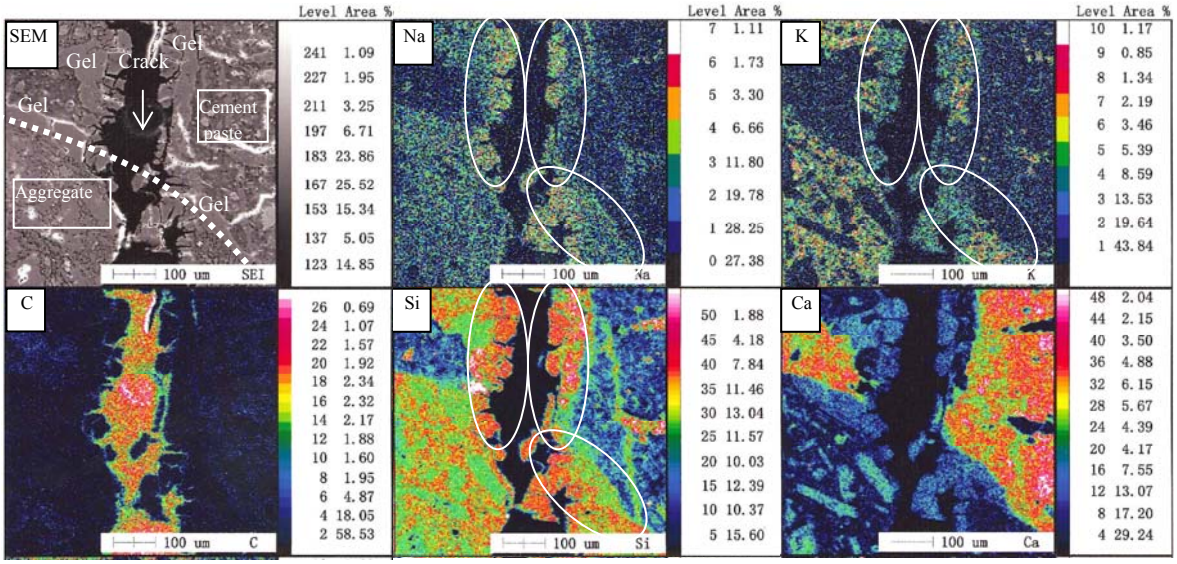

Figure 6: Elemental analysis on Na, K, C, Si and Ca in ASR gel, aggregate and sement paste in concrete by EPMA(EDS)

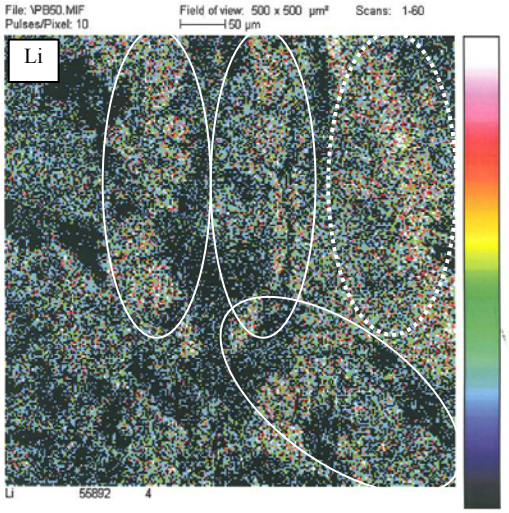

Figure 7: Elemental analysis on Li in ASR gel, aggregate and cement paste by TOF-SIMS

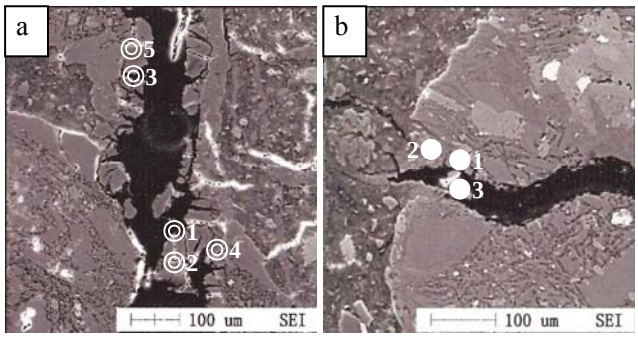

Figure 8: The positions of quantitative analyses : (a)ASR gel with Lithium ion, (b)ASR gel without Lithium ion

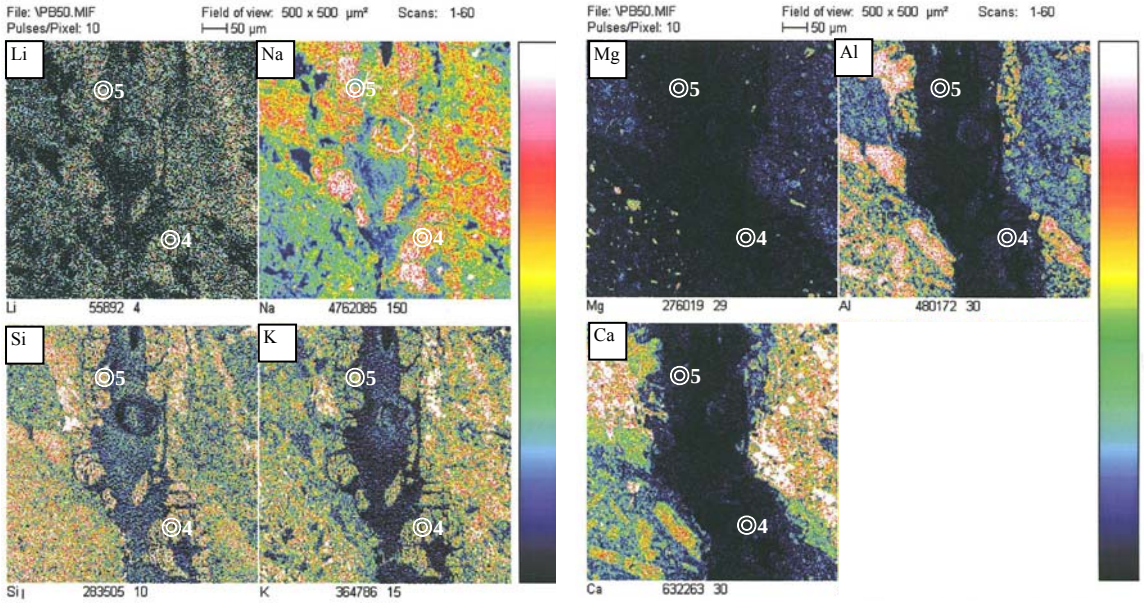

Figure 9: Elemental analysis on Li, Na, Si, K, Mg, Al and Ca in ASR gel, aggregate and cement paste in concrete by TOF-SIMS