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Damage to Cement Concrete Pavements due to Exposure to Organic Compounds in a Cold Region

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Abstract

Pop-out and disaggregation of aggregate in a one-year old cement concrete pavement originally mixed with air-entraining (AE) water-reducing agent was observed after the pavement had been exposed to ethylene glycol based snow-melting agent on the surface in the winter. The study used: Gas Chromatography Mass Spectrometry (GC-MS) tests, ¹H Nuclear Magnetic Resonance (NMR) tests, X-ray fluorescence analysis, Emission Spectral analysis (ICP), elution tests in anion type surfactant solution conducted for mortar and aggregate taken from the cement concrete where pop-out had occurred, as well as samples made by cement paste in the laboratory. Tests of the tensile strength, thermal–stress, and three dimensional crack analysis by micro focus Computerized Tomography (CT) scanner were conducted for specimens (2.5x2.5x10cm) taken from the cement concrete where pop-out had occurred and with cement concrete samples made in the laboratory. Microscope observations and Electron Probe Micro Analyzer (EPMA) analysis were conducted for thin samples (2.5 x 2.5 cm and 20 μm thick) taken from the cement concrete where pop-out had occurred. The tests results showed that organic compounds contained in the cement reacted with the cement during the hardening process, generating cracks and gel in the cement paste. It was established that these caused the pop-out of the aggregate, together with the effects of the ethylene glycol based snow-melting agent that the cement concrete had been exposed to. No pop-out or disaggregation of aggregate were found in cement concrete at a repaired section, at the same location, with aggregate of low absorbing water ratio in this cold region and in place for two years.

Key words: cement concrete pavement, pop-out, disaggregation, organic compounds, Gas Chromatography Mass Spectrometry (GC-MS), Electron Probe Micro Analyzer (EPMA), Micro Focus Computerized Tomography (CT) Scanner

1. Introduction

Modern cement concrete typically includes a complex mix of admixtures besides cement and aggregate and these may be the cause of Alkali Silica Reactions (ASR) [1] and [2]. Alkali compounds may be present in ingredients in the concrete or from external sources (deicing salts, ground water, and sea water), as changes in the Portland cement manufacturing processes have led to changes in the alkali content of cement. A number of mechanisms have been suggested to account for the pop-out of aggregate, including freezing and thawing effects [3-5], high absorption water ratios of aggregate, smectite in the aggregate [6-8], and organic compounds [9] and [10]. It has been observed that four types of aggregate (mud stone, tuffaceous siltstone, serpentine, and basalt-turned greenstone) in the kind of pavement considered in this paper have been involved in pop-out in actual concrete pavements. Expansive clay minerals are included in the mudstone and tuffaceous siltstone, while such minerals are not present in the serpentine and serpentine is not dissolved by ethylene glycol based snow-melting agents. There has been a number of reports [11] of pop-out of aggregate in one year old concrete pavements (30 cm thick) containing a lignin sulfate type air-entraining (AE) water-reducing agent, with the pop-out occurring four or five hours after spreading an ethylene glycol based snow-melting agent in winter. However, the mechanism of the pop-out of aggregate from the surface of concrete pavements has not yet been clarified [12-14].

This study aimed to identify causes of the pop-out phenomenon, and conducted a series of chemical and mechanical experiments using cement concrete samples collected from concrete in an actual concrete pavement. It was shown that the cement contained organic compounds that would originally be harmful to the cement and that these organic compounds reacted chemically with the cement during the hardening process. The organic compounds generated cracks and gel in the cement paste, and in combination with the effects of the ethylene glycol based snow-melting agent and

thermally induced cracks, caused the pop-out of aggregate. In the winter, snow-melting agent, an ethylene glycol type (same type of snow-melting agent in the field) had been spread on the surface of the cement concrete pavement of a section at the same location as the cement concrete pavement where pop-out was observed, but that had been repaired two years earlier, but here no pop-out or disaggregation of aggregate were found in this cement concrete with aggregate of low absorbing water ratio.

2. Experiments and test methods

Prior to the experiments to be reported below, it was verified that the application of phenolphthalein solution to the concrete cross sections cut from the concrete samples of the concrete pavements applied shortly after the cross sections were cut, neutralized the inner parts of the concrete specimens. With the cement concrete neutralized, it was believed that the strength of cement concrete would decrease. It has been confirmed [15] that pop-out phenomena are particularly common when certain aggregate types are used and that some of these types of aggregate dissolve with ethylene glycol based snow-melting agent solution and disaggregate under conditions of repeated freezing and thawing. However, the mechanism of the pop-out of the aggregate, which occurs four to five hours after snow-melting agent was applied to concrete pavements is not understood. To more fully understand this mechanism, a detailed examination using field samples of cement concrete pavements as well as laboratory samples was conducted.

First, the chemical component of the ethylene glycol based snow-melting agent was analyzed using ^1H NMR and GC-MS. Next, the influence of the surfactant contained in the ethylene glycol based snow-melting agent on aggregate and cement paste was investigated. In order to investigate the properties of the tensile stress and the thermal stress of a concrete sample, direct tensile and thermal stress tests were carried out. Further, to investigate the state of the cracks inside the concrete, micro

focus CT scan analysis and microscope observation were carried out. The organic matter contained in the concrete pavement was investigated using GC-MS. Furthermore, movement of the metal elements between aggregate and cement paste were investigated using EPMA and ICP.

2.1 Samples

2.1.1 Aggregate and cement

The aggregate and the cement used were the same as that used in the actual concrete pavements investigated. The cement was commercially available Portland cement, blast furnace and high-early-strength cement, from the same manufacturer as the cement actually used by the concrete pavement.

2.1.2 Concrete samples

Concrete samples made in the laboratory (Type A) and samples extracted from the actual concrete pavement (Type B) were used in this research. The compositions of the two kinds of cement concrete samples (Types A and B) are shown in Table 1.

The Type B samples were 2.5 by 10 cm sections of a 30 cm thick concrete pavement, cut into 2.5 cm thick samples, and numbered 0 to 8 from the top of the pavement. The samples were cut perpendicular to the surface of the pavement (Type B: 30 cm thick), in the moving direction of car travel (Type B) to check the longitudinal cracks in the pavement. The Type B samples were used for a direct tensile test, a thermal-stress test, CT, microscope observations, and EPMA. Type B samples were also crushed, and powder samples were made and used for GC-MS and ICP as will be described by the next section.

The Type A cement concrete was used only for the tensile and thermal-stress tests. The Type C cement concrete shown in Table 1 was from concrete placed at the same location as the Type B

samples, placed in a repaired section of a runway, and used for confirmation and elucidation of the pop-out phenomena reported in this study.

2.1.3 Powder samples

Samples were collected from the mortar and aggregate parts of the cement concrete pavement as well as from the mortar part around popped-out aggregate for GC-MS and Emission spectral analysis. Three types of powder samples were prepared by crushing these collected samples into 0.074 mm diameter or smaller particles using a hammer. In the following, these powder samples will be referred to as mortar powder (collected from the mortar parts), aggregate powder (collected from the aggregate parts), and scraped-out powder (collected from the mortar parts around popped-out aggregate) samples. Also, cement paste samples (ordinary Portland cement, water-cement ratio: 50 %, AE water-reducing agent of lignin sulfate type: 0.25 % of cement) were prepared and subjected to the GC-MS test, and the results were compared with the properties of samples collected from the actual concrete pavement (Type B). These samples prepared from cement powder were also crushed into particles of 0.074 mm or smaller in diameter using a hammer. These samples prepared from cement paste will be referred to as new-paste powder.

To examine the content of calcium dissolved by the surfactant solution using the various cement paste samples, normal Portland cement, blast furnace, and high-early-strength cement all from the same manufacturer were used to investigate possible differences in the properties of cement from the same cement manufacturer. The water-cement ratio of these cement paste samples was 50 %, and an AE water-reducing agent (lignin sulfate type) was added to the cement at a concentration of 0.25 %. The hardened cement samples were crushed into particles of 0.074 mm or smaller in diameter using a hammer and used in the experiments.

2.1.4 Thin samples

Using one of the concrete samples (Type B, sample No.2, 2.5 x 2.5 x 10 cm) described in Section 2.1.2, two thin samples (2.5 x 2.5 cm and 20 μm thick) were cut, 55.8 mm from one end of the 10 cm long sample (Z62 in the following), and 74.7 mm from the end of the same sample (Z83 in the following), using a water polishing method for microscopic observations.

2.2 Analyses

A number of techniques (12 types of tests) were used in the analysis of the concrete samples and powder samples and these are briefly are described next.

2.2.1 Nuclear magnetic resonance test

The nuclear magnetic resonance (NMR) test uses the phenomenon that nucleides divide into two energy states when placed in a strong magnetic field. The test produces a graph with peaks that allow chemical components of organic compounds in ethylene glycol based snow-melting agent to be identified based on the location and form of the peaks. The ethylene glycol alone did not cause the pop-out of aggregate, and it was assumed that other organic compounds in the ethylene glycol based snow-meting agent was involved.

2.2.2 X-ray fluorescence analysis

In X-ray fluorescence analysis the elements of the gel-like substances generated on the surface of aggregate when immersed in surfactant solution are identified, and this analysis was performed on the gel that developed on the concrete here.

2.2.3 Aggregate and cement concrete immersion test

Pop-out of the aggregate of concrete (Type B) pavement has been observed with only certain aggregate types. Therefore, the effect of the ethylene glycol based snow-melting agent and surfactant contained in additives in cement concrete on such aggregate and cement concrete was examined. A 10 % polyoxyethylene nonylphenyl ether sodium sulfate solution, a major anion surfactant, was used in this experiment. The use of the surfactant not only decalcified the cement paste but also generated a white gel-like substance around aggregate.

Cement concrete (Type B) samples were also immersed in water solution (10 % water solution of polyoxyethylene nonylphenyl ether sodium sulfate) for one week and a white gel-like substance was also observed here, now on the surface of samples. The samples (2.5x2.5x10 cm) were the same as those described in Section 2.1.2.

2.2.4 Elution test of cement-paste powder

New cement-paste powder (0.2 g) was added to water (400 ml), and after one week, the calcium and sodium contents in the solution were measured by chelate titration. The tests used 500 cc alkali glass beakers.

2.2.5 Chelate titration method

Substances that produce metal chelate compounds by forming coordinate bonds with metal ions are called chelating agents. A metal ion, M, which has dissolved in a solution and reacts with a chelating agent, Z, forms a metal chelate compound, MZ_x . This reaction occurs quickly and there are no side reactions. Then, if the amount of the titer of Z is measured, the amount of M will be known.

The content of calcium, water-soluble or refractory, in the solution generated by the immersion test for new cement paste was identified by this test method.

2.2.6 GC-MS

The GC-MS test was used to identify organic compounds in the powder samples. Three powder samples (mortar powder, aggregate powder, and scraped-out powder collected from concrete Type B), were extracted in a Soxhlet extractor. The samples were first extracted by methanol for 24 hours, and the residue was then extracted using chloroform for 24 hours [17]. The organic compounds were identified using GC-MS (gas chromatography-mass spectrometry)[18] and [19]. The same procedure was applied to the new-paste powder samples only here with direct extraction using chloroform for 24 hours.

Experimental conditions for the GC-MS are as follows: Column: HP-5, diameter 0.32 mm, length 30 m, film thickness 0.25 μm .

Thermal column conditions are as follows: 40-280 °C, 10 °C/minute; and Carrier gas: Helium, 1.5 ml/minute.

2.2.7 Tensile test

A direct tensile test was performed on the concrete samples (the 2.5 x 2.5 x 10 cm Type A and B samples) described in Section 2.1.2 with a dynamic load device (Modified Instron 1350, minimum deformation: ± 0.001 mm) at a loading rate of 0.043 mm/sec, and at ambient temperatures. The loads and deformations were measured at 100 Hz and the strength and fracture strain of the samples were calculated for both new and field samples (Type A and B).

2.2.8 Thermal-stress test

The dynamic load device in Section 2.2.7 was used in the thermal stress test, restraining both ends of the concrete samples (the 2.5 x 2.5 x 10 cm Type A and B samples). The pop-out of aggregate has been observed on actual pavements (Type B) in winter four to five hours after the application of a

ethylene glycol based snow-melting agent, and strictly speaking, thermal stress tests must be conducted at low temperatures. However, the temperature during the test (below +30 °C) was considered not to affect the test results as concrete is elastic. The cooling rate at ambient temperatures in the field are normally around 2 °C/hour, however, -10 °C/hour was adopted in this study as concrete is elastic, and as the higher cooling rate allows more accurate measurements.

2.2.9 Micro focus CT scanner (CT)

The CT was newly developed in this study. A cone-shaped X-ray (130 kV) beam was irradiated at the samples (Type B, Section 2.1.2, 2.5x2.5x10 cm) on a turntable, recorded by a detector (30 x 30 cm), and reconstructed in three dimensions. The resulting image was displayed in seven colors showing the three-dimensional shape distribution of voids. The crack (void) widths (multiples of 0.24 mm) were displayed with seven colors, red for the narrowest crack (0.24 mm), and wider cracks displayed with shorter wavelength colors. The cracks around the aggregate were analyzed using a micro focus CT scanner (X3DCT, JAZ-1300M) and software (VG StudioMAX 2.0 and ExFact Analysis for Porous/Particles 2.0) [16].

2.2.10 Microscope observation

Two parts (Thin samples: Z62, Z83), described as in 2.1.4, where cracks around aggregate were particularly large (in the second-layer [2.5 to 5 cm below the surface] sample [Type B] No.2) were selected based on the results of the three-dimensional crack shape analysis of Section 2.2.9. Two samples (Z62, Z83) were prepared by water polishing. The cracks and the gel-like substance near the aggregate, as well as the changes that had taken place in the aggregate, were examined using a microscope.

2.2.11 Electron Probe Micro Analyzer (EPMA) analysis

With EPMA it is possible to identify the metal constituents in thin samples. This enables an accurate identification and the ratio (density) of each constituent element of solid samples.

Carbon was applied to the thin samples (Concrete Type B, Section 2.2.10), and the elements in 2-3 μm diameter areas were identified using the QX200J installed in a JSM-T330A for the EPMA analysis.

2.2.12 ICP (Emission spectral analysis)

The amounts of SiO_2 , Al_2O_3 , CaO , K_2O , Na_2O , MgO , Fe_2O_3 , MnO , and P_2O_5 in the new-paste powder and the three powder samples were measured with an ICP emission spectrophotometer (ALS Chemix Ltd., Canada). The results, allowed a determination of whether or not changes in the constituents of oxides such as calcium occurs around aggregate in the samples and the content of organic compounds by the loss occurring at heating .

3. Results and discussion

3.1 Chemical constituents of the snow-melting agent

Experiments (^1H Nuclear Magnetic Resonance [^1H NMR] and GC-MS) with the ethylene glycol based snow-melting agent found that it contained two anion type surfactants – second potassium phosphate and sodium-di (2-ethylhexyl) sulfosuccinate in addition to ethylene glycol. Based on this it was decided, to use polyoxyethylene nonylphenyl ether sodium sulfate, an anion surfactant, in the immersion experiments, as this would cause the elution of the calcium in the cement concrete, which would turn the solution cloudy, showing when calcium salts were generated [17] and [20].

3.2 Immersion experiments of cement concrete and aggregate in the ethylene glycol based

snow-melting agent

The cement concrete samples (Type B, Section 2.1.2) were immersed in 10 % ethylene glycol based snow-melting agent. The samples contained mudstone, serpentine, and tuffaceous siltstone, three aggregate types with similar lithologic characteristics and origin as those that popped out in the actual concrete pavement. The immersion of the cement concrete and the three aggregate samples all made clear water cloudy, indicating that calcium in the cement concrete (Type B) and the aggregate was eluted. Microscopic observations of the thin samples confirmed that the mudstone did not contain illite, the tuffaceous siltstone did not contain illite or micro quartz, and that the serpentine contained none of the two – these are substances that would cause alkali-aggregate reactions. It was also confirmed that while expansive clay minerals were present in the mudstone and in the tuffaceous siltstone, the microscopic observations of thin samples showed no expansive clay minerals in the serpentine.

In summary, it was confirmed that the mortar and some of the types of aggregate in cement concrete Type B caused the rapid depletion of calcium as a result of the application of the ethylene glycol based snow-melting agent. This suggests that the cement paste used in the cement there contained organic compounds.

3.3 Immersion of aggregate in a surfactant solution

A white gelatinous substance was formed around the aggregate just after the immersion in 10 % polyoxyethylene nonylphenyl ether sodium sulfate solution as described in Section 3.2. When the white gelatinous substance around the aggregate dried, it shrank. The dried substance was subjected to X-ray fluorescence analysis to determine its constituents. Based on the radical constituents (Table 2), the calcium component in the aggregate had been eluted (see Table 3). The metal elements of the aggregate were measured by the ICP emissions of the light spectroscopic analysis (Table 2). Mudstone,

serpentine, and green mudstone in the anion type surfactant solution were eluted abundantly and in a short time (Table 3). It was confirmed that they form a gelatinous substance and that this attached around aggregate in this experiment. The anion type surfactant included in the ethylene glycol based snow-melting agent reacts with the aggregate in the cement concrete and causes the depletion of calcium in the aggregate and this depletion results in damage such as the pop-out to the cement concrete in a short time. Therefore, it is suggested that the cement paste in concrete Type B contained organic compounds.

It would appear likely that ion exchange reactions between the calcium ions in the aggregate and the anion ions in the surfactant occurred in the phenomena described in this section.

3.4 Elution experiment with cement-paste powder

High-early-strength cement paste with and without an AE water-reducing agent was made and after setting the product was crushed by hammer, to dissolve more easily in watery solutions, and the crushed product was immersed for one week in either of an anion surfactant solution (0.5 %), a nonionic surfactant solution (0.5 %), or distilled water to examine the content of calcium salt eluted into the water solution, with the results shown in Fig. 1. The watery solutions were cloudy soon after immersion (90 minutes) of the crushed cement-paste powder and this was particularly the case with the anion type surfactant water solution. At the end of the one week immersion, the solutions were strained through a paper filter (0.8 μm) to separate refractory calcium and water-soluble calcium. The calcium contained in the strained solutions was defined as water-soluble calcium, and the calcium left in the filter or attached to the surface of the beaker (the beaker used was alkali glass, and ion exchange with Ca^{2+} and the sodium ions occurs at its surface) was defined as refractory calcium (Figure 1). It is assumed that the water-soluble calcium is eluted out by the surfactant and causes the cracks

around the aggregate in the cement concrete. The contents of both kinds of calcium was measured by Chelate titration.

Figure 1 shows that the most calcium in the new cement paste was eluted by the anion type surfactant solution after one week and approximately similar amounts of water-soluble and refractory calcium were eluted in the anion type surfactant solution. Therefore, from the results in Figure 1, it is considered that a part of the cement paste in the cement concrete pavement turned to water-soluble calcium in water and that it was eluted.

Anion or non-ion type surfactant is generally used in AE water-reducing agents and for same purposes. Next, the effect of both surfactants on new cement paste was investigated. The quantity of calcium eluted from the cement-paste powder in the non-ion type surfactant solution was smaller than that eluted in the anion type surfactant solution and the quantity of refractory calcium was slightly larger than that of water soluble calcium in Table 4. It was concluded that the depletion of calcium involves factors additional to the concentration of calcium in the cement.

It may be considered that an anion type surfactant like the AE water-reducing agent (salt type, premixed with the cement) and ethylene glycol based snow-melting agent including anion type surfactant rapidly causes the depletion of calcium by chemical reactions such as hydrolysis.

When AE water-reducing agent is added to cement, the amount of calcium eluted, regardless of the kind of surfactant, increases immediately (Figure 1). Table 2 shows that the quantity of calcium oxide in the cement-paste powder samples with or without of AE water-reducing agent was 49.2 - 56 % by ICP emission light spectroscopic analysis. Table 4 shows the quantity of calcium eluted in one week in relation to the gross weight of the calcium and the quantity of calcium eluted from the cement-paste powder depends upon the type of cement and whether or not AE water-reducing agent has been added.

In conclusion it was established that the calcium in the cement paste turns water-soluble or becomes

refractory calcium salt when eluted. This is most pronounced when the AE water-reducing agent and anion surfactants are both present (Table 4). It may be hypothesized that the water soluble calcium salts were rapidly dissolved out from the pavement when the deicing agent was applied and that this created voids in the pavement.

3.5 Component analysis by GC-MS

The GC-MS spectra with the peaks for organic compounds in the aggregate powder, are shown in Figure 2, for the mortar powder in Figure 3, and for the new-paste powder in Figures 4 and 5.

Various phthalate ester compounds were identified in the aggregate powder, and it is thought that these compounds were attached to the surface of the aggregate or penetrated into the aggregate, or that they originated in the cement paste around the aggregate which was not completely removed.

Experiments, that examined the presence or absence of AE water-reducing agent in the new-paste powder, showed that the GC-MS spectra were almost the same as the DOP (di-octyl phthalate) and DEP (di-ethyl phthalate) spectra both with and without the AE water-reducing agent. These organic compounds, which were obtained from new cement paste and aggregate powder, as well as from mortar powder using GC-MS, are listed in Table 5. It is suggested that a part of the organic compounds (ester of phthalate, such as the DBP, DEHP) in the aggregate powder changed to other compounds (DMP, di-methyl phthalate) by chemical reactions. These experiments suggest that the commercially available Portland cement originally contained phthalate ester, ester hydrocarbon, and diethylene glycol. The former two compounds are ester type and the latter is a polyol-based fatty acid ester compound. It is suggested that the organic compounds identified, other than diethylene glycol, may be associated with the thermal recycling techniques used in cement production, which utilizes organic compounds such as industrial waste and industrial byproduct. This suggests that DBP, DEHP, and other compounds are included in waste, as byproducts, and that such organic compounds are left

in the manufactured cement.

3.6 Tensile tests of the cement concrete

Figure 6 shows the results of the tensile tests for both Types A and B concrete. While almost no differences were found in tensile strength of the two samples (Type A and B) prepared as described in Section 2.1.2, the fracture strain differed markedly in the two samples. A large strain occurred because the elastic modulus (gradient) of the stress-strain curve in the initial stages was $1.2 \times 10^5 \text{ kg/cm}^2$ ($1.2 \times 10^4 \text{ MPa}$), smaller than that of new cement concrete (Type A) made in the laboratory ($3 \times 10^5 \text{ kg/cm}^2$, [$3 \times 10^4 \text{ MPa}$]). It was suggested that the differences in fracture strain was caused by cracks around the aggregate, according to microscope observations and CT scanning. Figure 6 shows that the stress-strain curves for both concrete samples (Type A and B) deviate from a straight line (elastic body) after a strain of 0.01 % (100×10^{-6}) (red vertical line in Figure 6). Beyond a strain of 0.01% the curve bends because of the presence of inner cracks, indicating the plastic characteristics of the concrete, and it subsequently has a shape that indicates a large fracture strain, 0.04 % (400×10^{-6}), in concrete Type B.

It was confirmed that a crack was observed in the aggregate when CT scanning was performed on a fractured sample (Type B) after this experiment. Therefore, the cement paste present here suggests that cracks formed around aggregate when this cement concrete hardened so that there is a shrinkage distortion of 1 % ($10,000 \times 10^{-6}$) in the cement paste as described below.

3.7 Thermal stress tests of the cement concrete

Figure 7 shows thermal stress-temperature curves obtained with the Type A and B samples described in Section 2.1.2. It appears that a crack has already formed in the cement concrete (Type A and B) at this difference of temperature (from 30 °C to 25 °C) suggesting that the stress-temperature

curve curves from a difference in temperature of around 5 °C (red vertical line in Figure 7). This means that cement concrete does not show elastic behavior after this zone. Both concretes (Type A and B) fractured at around 10 °C (red vertical line shown in Figure 7) differences in temperature (from 30 °C to 20 °C). With a linear coefficient of expansion of cement concrete of $1 \times 10^{-5}/^{\circ}\text{C}$, the strain of the cement concrete (Type A and B) at the point where the thermal crack occurs is 0.005 % (50×10^{-6}) (5 °C), and the fracture strain is 0.01 % ($1 \times 10^{-5}/^{\circ}\text{C} \times 10^{\circ}\text{C} = 100 \times 10^{-6}$).

A CT scan was performed on the Type B sample after the thermal stress experiment (fracture strain: 1.2×10^{-4} , 0.012 %) to observe possible internal cracks in the sample, it was confirmed that a crack had occurred between the surface and cement paste of the aggregate.

The pop-out phenomenon in the cement concrete (Type B) pavement occurred four or five hours after spreading the ethylene glycol based snow-melting agent on the concrete pavement in the winter here. Considering the above test results, the pop-out was very possibly caused by newly formed cracks caused by the sudden cooling (four or five degrees) of the pavement surface by the application of the ethylene glycol based snow-melting agent.

It has been reported [21] that the contraction of a cement paste sample (4 x 4 x 15 cm) without additives stopped in 30 days at a strain of 1 % ($10,000 \times 10^{-6}$) and that the strain of contraction of cement paste with multifunctional water-reducing agent (ester and/or ether type) which stopped at 90 days was 1 % ($10,000 \times 10^{-6}$) or more, but that contraction did not stop at this time, indicating that chemical reactions were still occurring in the cement concrete.

Miyaguchi (2002) showed that the addition of additives not only slowed the contraction but also increased the total amount of contraction in cement paste [21]. The 1 % strain exceeds the fracture tensile strain and fracture strain of the thermal stress of cement concrete (Types A and B) shown in Figures 6 and 7. Ester and salt type compounds cause hydrolysis under strongly alkali conditions, and such compounds are well known to change into alcohols, acids, and similar compounds.

In a laboratory experiment it has been confirmed that phthalate ester and/or ester hydrocarbon initiated chemical reactions with calcium in cement concrete at ambient temperatures within a short period of time generate calcium salts [18] and [19].

These various findings suggest that chemical components harmful to cement bring about chemical reactions, such as hydrolysis, in cement concrete during the hardening process (within about 90 days) in the short term, and that this contracts the cement paste and creates cracks.

When the Type B cement concrete was cut using a diamond cutter, the following unexpected and notable phenomenon was observed. When phenolphthalein liquid was sprayed on the cut section of concrete, no pink color was observed on the surface of the cut concrete and the cross section was neutralized. This cement contained an additive of lignin-sulfate and polyol compounds (AE water-reducing agent, Pozzoloth No.70), a type of ester compound in which acids and alcohols are linked. This is similar to an ester type surfactant linked with anion type surfactant and alcohol and various ester compounds which are then present in the cement from the mixing stage. In addition, because diethylene glycol is an ester type organic compound, hydrolysis of the esters and ion exchange reactions, in a short time, produced calcium salt in the presence of water when the cement concrete was cut and with the highly alkali conditions of the cement it is thought that the neutralization of the cement concrete was promoted in a short time in this manner.

3.8 Three-dimensional crack analysis

The cement concrete sample collected from the actual concrete pavement (Type B, Section 2.1.2) was cut into nine slices (2.5 cm thick each, in the following samples No.0 to 8) from the pavement surface to the bottom of the pavement. The samples were examined using a micro-focus CT scanner (CT in the following), and the three-dimensional crack analysis was performed using special software (VG Studio Max 2.0 and ExFact Analysis for Porous/Particles 2.0) to examine the internal void

distribution.

The three-dimensional void distribution in the cross sections of the concrete pavement (Samples No.0-8) (Photo 1 shows six of these) shows many cracks throughout the concrete (from the surface to the bottom). In Photo 1, red indicates cracks of 0.24 mm, orange 0.48 mm, yellow 0.72 mm, green 0.96 mm, blue 1.2 mm, indigo 1.44 mm, and purple 1.68 mm. As shown in Photo 1, the first sample (No.0: 0- -2.5cm from the surface) had many cracks in red (0.24 mm wide) around some of the aggregate; however, the second and deeper layers had cracks around all aggregate of diameter 5 mm and larger, showing intense crack formation in the deeper layers. The reason for the first layer having fewer cracks around aggregate may be that the smaller void content (8.2 %) of the shallow (near the road surface) layers resulted in the separation of concrete (mortar and aggregate) and the AE water-reducing agent (specific gravity: 1.06) at placement, because of the vibrations arising during the placement of the cement concrete shown in Photo 1.

These results suggest that the cement concrete (Type B) already had many cracks around the aggregate in the deeper parts during hardening, from when it was placed, one year before the sample collection.

The cracks around aggregate in the Type B concrete (Photo 1: sample No.1, layer No. 2) shows a cavity detailed by the arrow in the Photo 2a CT image. Photo 2b shows a color image for the same sample (sample as in layer No.1), but showing the other side of the sample. The white bands around the aggregate in same sample (layer No. 1 Photo 1) can also be observed here.

A white-woolen-muffler-like formation shown in Photo 4a around aggregate in the concrete sample (No.2, Third layer) particularly in the black and white image (two dimensional image of CT) was observed. Phenomena like this muffler like formation were observed in both the three dimensional void distributions in Photo 1 and in the black-and-white CT images (images

taken in three directions: perpendicular to the surface (direction X), at a right angle to the sides (direction Y) and along the end surfaces (direction Z)). The white aggregate, the cirrocumuli-like surface, and the white-woolen-muffler-like patterns around aggregate were mainly observed with greenstone, mudstone, and serpentine, and crack-line patterns around aggregate were observed in all these cases using the two dimensional black-and-white images of CT. The pop-out of aggregate was remarkable in mudstone and serpentine. The type of aggregate was confirmed by observations by lupe. Cracks (black) around aggregate in concrete Type B, confirmed in the black-and-white CT images, were found with basalt-turned-greenstone (GBS), basalt-turned-hyaloclastite (GHY), transformed mudstone (TMS) and gabbro-turned-greenstone (GDO), and also mudstone (MS). Also, black-and-white two dimensional CT images showed that cracks (in this case: white) were present in most of the white parts, observable with the naked eye, around aggregate (see Photo 2b). In the black-and-white two dimensional CT images shown in Photo 2a, voids surrounding aggregate, not the aggregate themselves, appeared black (void: black in the CT images indicates the existence of air pockets), and large voids around the aggregate were also confirmed (Photo 2a, 2b).

When the six samples (concrete Type B, from No.0 to 5 and No.8) taken from the pavement were examined manually, many cracks were found around the GBS aggregate and the aggregate appeared to have changed color. While TMS aggregate (transformed mudstone) itself did not change color, there were voids around this aggregate. Such voids beneath the aggregate were observed only in the shallow parts of the concrete pavement (near the pavement surface).

The voids beneath the aggregate near the pavement surface were confirmed by subjecting sample No.0 (Photo 1) to CT scanning and rotating (to see the three dimensional crack distribution around the aggregate) the three-dimensionally analyzed images (Photos 3a and 3b). When the concrete sample (Type B) was cut and the cross section was observed with the naked eye, the cement paste around the

aggregate with voids beneath them had white, ring-shaped patterns, whereas the aggregate itself did not change color. In addition, a crack around this kind of aggregate forms a linear crack which seems to be part of a net and that is not a crack of the plane type (Photo 3b).

According to past site observations, the pop-out of aggregate is typically observed with mudstone, tuffaceous siltstone, and serpentine. Except serpentine, these kinds of rock contain expansive clay minerals (smectite) and other minerals that cause alkali-aggregate reactions. The cement paste around fine tuff and serpentine aggregate was neutralized and gabbro, fine sandstone, and basalt-turned-greenstone, which have not been observed to take part in pop-out phenomenon do not contain expansive clay minerals (smectite). Gabbro does not contain minerals that cause alkali-aggregate reactions either. Reaction rims were not observed around fine-sandstone aggregate, which were subject to an alkali-aggregate-reaction causing illite.

Four types of aggregate, serpentine, peridotite, un-transformed sandstone, and mudstone, are known to react with the ethylene glycol based snow-melting agent used on pavements. This aggregate may turn into mud when reacting with ethylene glycol based snow-melting agents. The reason for the pop-out aggregate turning to gravel (disaggregation) may be the reaction of the aggregate with the ethylene glycol based snow-melting agent.

Also, the CT images confirmed that some parts around the aggregate in concrete Type B (sample No.2, second layer) and the aggregate itself appeared white (see Photos 4a and 4b). The reasons for the parts surrounding the aggregate turning white, the surface (cross section) of the concrete presenting a pattern that looks like cirrocumuli clouds and the rims of the aggregate turning indistinct, may be that smectite in the aggregate reacted with additives (surfactants) and sodium in the cement, and then the reaction products reacted with calcium in the cement, generating calcium salts (see Table 6 and Photo 4a).

Since it is generally accepted that alkali-aggregate reactions do not occur in serpentine, an aggregate

connected with the pop-out, and serpentine contains few expansive clay minerals, the cracks that occur around the aggregate may be due to chemical reactions between the surfactants in snow-melting agents and/or ester type compounds present in the cement and aggregate or cement paste, accompanying decalcification.

Based on the analysis of the CT images, it was suggested that an ion-exchange reaction occurred both on the surface and inside the aggregate in all the layers of the 30-cm-thick concrete pavement, which was in contact with the cement paste around the aggregate, creating fine cracks. The analysis also shows that such fine cracks were not observed in old cement concrete (30 years ago) by CT images, but in the samples reported here many cracks were confirmed in black-and-white CT images around aggregate in the concrete samples (Type B) at all depths, and the voids beneath certain aggregate were particularly large in the fourth-layer (Type B, sample No.3, green or blue lines).

Based on these results, it was suggested that the many cracks in the pavement concrete, as shown in Photo 1, were not caused by alkali-aggregate reactions but by the weak adhesion between aggregate and paste, which caused cracks around aggregate when thermal stress occurred in the cement concrete, and the surfactants in the snow-melting agent penetrated into these cracks and chemically reacted with the cement paste, generating the white rings (calcium salts), observable with the naked eye, around aggregate in the cement paste. The authors [17] have reported that when anion surfactant and calcium in cement react chemically, the calcium is eluted (the part that turns white), turning the concrete into gravel.

3.9 Microscopy

Micrographs of the thin samples (concrete Type B, sample No.1, Thin sample: Z62, Z83) collected from two parts of the second-layer sample (depth:-2.5- -5.0cm) are shown in Photos 6, 7, and 8.

Cracks were observed around mudstone (Photo 6) and reaction rims (RR) were also observed around

the aggregate. The WB indicates the white reaction rim in the cement mortar and the widths of the rims was 0.4 mm or less. This outbreak of cracks suggests that it was in a state just before the pop-out would occur. It is considered that the results show that an alkali-aggregate reaction may have occurred in the cement concrete pavement, this reaction may be an alkali-silica reaction or an alkali-carbonate reaction [22] and [23].

3.10 Electron Probe Micro Analyzer (EPMA) results

Figures 8, 9, and 10 show the constituents of oxides (%) in the aggregate and cement paste based on EPMA findings around the points indicated in Photos 6, 7, and 8 respectively, as also detailed in Section 3.9. The results show that there is movement of the constituents of the oxides between aggregate and cement paste. Silica was eluted from mudstone and adhered to hardened cement paste as shown in Figure 8. Calcium was eluted from cement paste and was present in the white bands. Further, silica was eluted from aggregate and cement paste around the basalt which became greenstone as shown in 9. Here the calcium oxide content increased slightly in the white bands (compared with the content in the cement paste) and formed a white band or the outermost of the reaction rim of the aggregate. The results in Figure 9 show that the oxides of aluminum, sodium, and potassium were concentrated in the outermost part of the reaction rim of the greenstone and that these are also present in the white band.

Silica oxide in chert aggregate (Z62C in Figure 10) and in the hardened cement paste were eluted and moved to the system outside. The calcium salt (water-soluble calcium) was eluted, and both calcium and silica decreased, because the calcium salt (water-soluble calcium) was eluted when the sample was polished (and water was used in the polishing).

The calcium of the cement paste (refractory calcium) increased, compared with the concentration around the mudstone (Z62A in Figure 8) and calcium was present in the white band. The oxides of

aluminum and sodium increased around the chert (Figure 10).

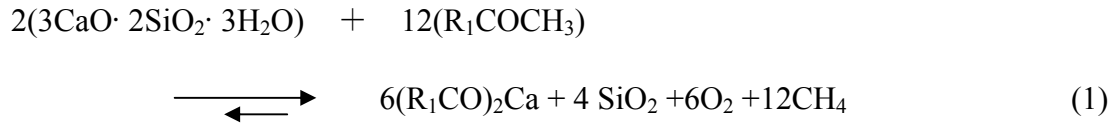
The metal element ingredients of basalt-turned-greenstone in the cement concrete pavement were changed, especially the oxides of silica, aluminum, iron, and calcium are shown in Figure 9 (see Photo 7).

These results suggest that cracks occurred around the aggregate, white reaction rims occurred in the peripheral parts of cement paste, and that the content of calcium oxide in these reaction rims was markedly different from that in the periphery of the cement paste. Despite the differences by aggregate type in the cement paste and periphery of aggregate, chemical changes occurred in these parts (periphery of cement paste and aggregate).

3.11 Analysis of metal oxide constituents

The constituents of the metal oxides in the aggregate powder (column 1 in Table 7), mortar powder (column 2), and scraped-out powder collected from the cement concrete at the site of the pop-out (column 3), and the new-paste powder (column 4) are shown in Table 7. The mortar powder and scraped-out powders contained more aluminum, magnesium, and sodium but less silica, iron, and calcium than the new-paste powder. The contents of calcium oxide in the mortar powder and scraped-out powders and the new-paste powder were very different. Specifically, the contents of calcium oxide in the scraped-out powder were very low, and microscopic and X-ray fluorescence analysis showed that it contained considerable quantities of calcspar. The calcspar may be hypothesized to have been generated in the neutralization of the cement paste. Parts of the cement mortar around aggregate which took part in the pop-out were neutralized and eluted in the calcium salt.

This finding suggests that the ester compounds undergoes a chemical reaction with the main ingredient of the cement, $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ (C-S-H), according to the following,



In addition, there is an ion exchange,



It may be assumed that calcium salt and silica were generated from the cement paste by these chemical reactions, and the results suggest that the chemical reactions between ester compounds or anion type surfactants such as the AE water-reducing agent and the cement paste occur rapidly.

It is therefore suggested that the gel in the white band in the cement paste around the aggregate is generated by chemical reactions between cement paste and the organic compounds originally present in the cement and the gel caused the cracking. This gel, together with the gel generated by penetration of ethylene glycol based snow-melting agent due to thermal stress, in a short time caused the pop out of aggregate from the surface of the cement concrete pavements.

The ignition loss by heating (LOI) of the cement paste of the deteriorated cement concrete (Type B:14.9 % included with the water content) was much larger than with new cement paste (JIS R5211: 3.0 % or smaller) as shown in Table 7. It is also confirmed that the organic compounds in the cement paste of concrete Type B is harmful to cement concrete.

4. Conclusions

This study investigated the pop-out phenomena of aggregate from the surface of concrete pavements. The pop out occurred after exposing the pavement to ethylene glycol based snow-melting agent in the cold season, and the investigation used a variety of chemical and mechanical tests. The following conclusions may be drawn for the Types A, B, and C concrete (Type A are samples prepared

in the laboratory, Type B are samples of a one year old concrete pavement, and Type C samples are from a pavement section at the same location as the Type B samples but which had been repaired two years previously) :

- 1) The mudstone, serpentine, tuffaceous siltstone, and green mudstone, which were involved in the pop-out phenomena, displayed rapid dissolution by the action of an anion type surfactant and an ethylene glycol based snow-melting agent, and formed calcium salt gels. This gel formation phenomenon was also observed in Type B concrete containing these rock types as aggregate.
- 2) The calcium constituent of cement paste around aggregate in Type B cement concrete was eluted by the anion type surfactant and formed white bands around the aggregate.
- 3) The calcium constituent in the cement paste is easily eluted by surfactants and turns into water-soluble and/or refractory calcium. Water-soluble calcium was eluted out as part of a calcium salt and this formed voids around the aggregate. The refractory calcium formed gel and/or calcspar and this is the cause of the decalcification of the cement concrete.
- 4) The calcium constituent in the new cement paste involved with AE water-reducing agent was more rapidly eluted by anion and non-ion type surfactants than that without AE water-reducing agent. Ester type hydrocarbon and/or ether type compounds in cement paste rapidly decrease the content of calcium in cement paste.
- 5) White aggregate, cirrocumuli-like and white-woolen- muffler -like patterns around aggregate, which were observed by micro-focus CT scanner, were mainly observed in greenstone, mudstone, and serpentine, and crack-line patterns around these kinds of aggregate in Type B concrete were observed in all these cases.
- 6) The cement (without an AE water-reducing agent) contained phthalate ester and ester hydrocarbon from the beginning. These are harmful to cement. The cement paste in Type B concrete contained 14.9 % of organic compounds, including water content.

- 7) The maximum tensile strength of the Type B cement concrete was around 15 kg/cm^2 (1.5 MPa) which was not significantly different from the new concrete samples (Type A); however, the fracture strain of Type B cement concretes was much larger than that of Type A cement concrete due to the presence of cracks.
- 8) The gradient of the stress-strain curve in the tensile test for new cement concrete (Type A) was small in the initial stages and the stress-strain curve for both concrete samples (Types A and B) is not a straight line after around 100×10^{-6} (0.01%) of strain.
- 9) Cracks around aggregate in Type B cement concrete occurred at a temperature differences of a mere 5-6 °C by thermal stress due to the decrease in temperature by spreading the snow-melting agent.
- 10) Fine cracks occurred around aggregate in the Type B concrete, and some aggregate near the surface of the cement concrete pavement already had voids beneath the aggregate, and the shape of the voids can be observed in certain aggregate types using three dimensional void analysis and CT scanning.
- 11) The Micro-focus CT scanner is a very useful tool to check for the presence of cracks in three dimensions in cement concrete.
- 12) The movement of metal constituents in Type B concrete was observed to be very active in the aggregate and cement mortar, using EPMA analysis. The loss of calcium along the rims of cement mortar was particularly noticeable.
- 13) The results suggest that the ethylene glycol based snow-melting agent penetrated easily into cracks due to thermal shrinkage around aggregate in the Type B cement concrete, this resulted in the formation of gel in the cement paste together with phthalate ester and ester type hydrocarbon in new cement paste, causing the pop-out of the aggregate.
- 14) Cement concrete pavement (Type C) with aggregate of low absorbing water ratio was found not to

exhibit pop-out of aggregate in cement concrete at a repaired section at same place in the cold area for two years after placement.

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Table 1 Compositions of cement concrete (Type A, Type B and Type C), absorbing water ratio, type of rock of aggregate and type of AE water-reducing agent

Concrete Type	Material	Ratio in weight (%)	Absorbing water ratio(%)
Type A (Laboratory)	High-early-strength cemen	18.8	
	Water	7.1	
	Crushed stone (5-20 mm)	43.0	1.05
	Sand	31.1	1.65
	Water/cement	41.0	
	Ratio of fine aggregate	42.2	
	Slump (cm)	13.0	
AE water-reducing agent (Lignin sulfate and Polyol compounds type: Pozzoloth No.70, Content:0.25% x Cement)			
Type B (Field)	Normal Portland cement	17.6	
	Water	7.4	
	Crushed stone (5-20 mm) ¹	35.7	1.05
	Sand	39.3	1.65
	Ratio of fine aggregate	36.8	
	Slump (cm)	2.5	
AE water-reducing agent (Lignin sulfate and Polyol compounds type: Pozzoloth No.70, Content:0.25% x Cement)			
Type C (Repaired section: Field)	Normal Portland cement	12.7	
	Water	5.5	
	Crushed stone	53.2	
	(20-40 mm) ²		0.32
	(5-20 mm) ³		0.31
	Sand	28.6	1.65
	Ratio of fine aggregate	35.8	
	Slump (cm)	2.5	
AE water-reducing agent (Denaturalized lignin sulfate type: Pozzoloth No.78S, Content:0.25% x Cement)			
1: Main rock: Basalt-turned-greenstone(GBS), Gabbro-turned-greenstone(GDO), Granite, Transformed sand stone(TSS), Gabbro(GAB)			
2: Main rock: Diabase			
3: Main rock: Limestone			

Table 2 Constituents of oxides (%) in aggregate and cement determined by X-ray fluorescence analysis

	Rock				Cement		
	Mudstone	Serpentine	Basalt*	NPC ¹	HESC ²	HESC+AE ⁴	BFC ³
SiO ₂	72.1	38.3	47.2	17.1	16.5	16.9	21.4
Al ₂ O ₃	9.4	2.0	12.3	4.5	4.1	3.9	7.3
Fe ₂ O ₃	4.3	8.0	14.8	2.3	2.3	2.3	1.7
Mn ₂ O ₃	0.1	0.1	0.2	0.1	0.1	0.1	0.2
MgO	1.5	33.5	5.1	1.3	1.4	0.9	3.0
CaO	1.1	0.4	9.0	55.0	56.0	56.3	49.2
Na ₂ O	1.3	0.1	2.9	0.2	0.2	0.2	0.2
K ₂ O	1.5	0.0	0.2	0.4	0.3	0.3	0.3

*: Basalt: Basalt-turned-greenstone (GBS)

1: Normal Portland Cement (NPC) 2: High-early-strength cement (HESC)

3: Blast furnace cement (BFC) 4: AE water-reducing agent (AE)

Table 3 Constituents of metal (%) of the gel-like substance around aggregate generated in the surfactant solution*

	Surfactant*	Mudstone	Serpentine	Basalt-turned-greenstone
Na	21.0	10.9	15.8	17.5
S	79.0	61.8	66.7	55.5
Mg		1.6	-	-
Si		1.5	0.5	1.7
K		1.1	0.3	1.1
Ca		22.7	16.1	25.3
Fe		0.4	0.6	2.0

*Surfactant: Polyoxyethylene nonylphenyl ether sodium sulfate (10% solution)

Table 4 The quantity and ratio of the calcium vs. the post-eluted calcium contents of the cement paste (one week immersion)

	HESC ¹			HESC+AE ³			BFC ²	
	Water	No-nion	Anion	Water	No-nion	Anion	Water	Anion
De-calcium (mg)	74.2	48.5	94.2	56.1	60.2	120.3	52.1	66.2
Ratio (%)	66.3	43.3	84.1	50.1	53.8	107.4	52.9	67.3

1: High-early-strength cement (HESC)

2: Blast furnace cement (BFC)

3: AE water-reducing agent

Table 5 List of compounds in aggregate powder, mortar powder and new-paste powder in concrete type B using GC-MS

Aggregate powder	DBP, DOP, DMP, (2,2-Dichloro-1-methylcyclopropyl)benzene, Hydrocarbon group
Mortar powder	DOP, Hydrocarbon group
New-paste powder	DBP, DOP, DEHP, Ethyl oleate, Ethyl palmitate, Ethyl stearate, Alcohol, Hydrocarbon, Diethylene glycol, 1-hexadecanol, Ethylester organic acid (estimated)

Table 6 Substances and compounds determined from black-and-white CT images and naked-eye observations for concrete type B

Very white aggregate	Transformed sand stone(TSS),Transformed mudstone (TMS), Basalt-turned-greenstone(GBS),Basalt-turned hyaloclastit(GHY), Basalt(BS),Gabbro-turned-greenstone(GDO)
Grey aggregate	Transformed sandstone(TSS), Transformed mudstone (TMS), Basalt-turned-greenstone(GBS), Basalt(BS), Mudstone(MS)
Cracks around aggregate	Transformed mudstone(TMS), Basalt-turned-greenstone(GBS), Basalt-turned hyaloclastit(GHY), Gabbro-turned-greenstone (GDO), Mudstone(MS)
White rim observed by the naked eye	Basalt-turned-greenstone(GBS), Basalt-turned hyaloclastit(GHY), Transformed mudstone(TMS)

Table 7 Results of the chemical analysis of powder samples for concrete Type B

Sample No.		No. 1	No. 2	No. 3	No. 4
Sample name		Aggregate powder	Mortar powder	Scraped-out powder	New-paste powder
Note		Aggregate of deteriorated part (Concrete Type B)	Cement mortar of deteriorated part (Concrete Type B)	Reaction zones that contact with aggregate (Concrete Type B)	Normal Portland Cement
Oxides and others	SiO ₂	53.8	33.4	38.2	17.1
(Percentage by weight)	TiO ₂	0.42	–	–	–
	Al ₂ O ₃	14.4	8.35	8.98	4.5
	Fe ₂ O ₃ *	7.86	5.66	5.84	2.3
	Cr ₂ O ₃	0.05	–	–	–
	MnO	0.12	–	–	–
	Mn ₂ O ₃	–	0.11	0.11	0.1
	MgO	6.07	2.8	3.25	1.3
	CaO	10.35	31.4	22.5	55.0
	BaO	0.02	–	–	–
	SrO	0.02	–	–	–
	Na ₂ O	2.52	1.03	1.39	0.24
	K ₂ O	0.57	0.57	0.7	0.36
	P ₂ O ₅	0.1	–	–	–
	SO ₃	–	1.0	0.7	–
	LOI	3.93	14.91	NSS	–
	P (ppm)	–	780	660	350

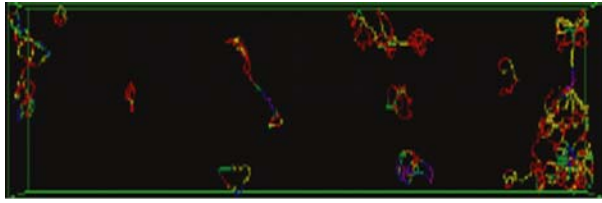
Analysis method: ICP emission spectral analysis

*Total iron calculated as Fe₂O₃

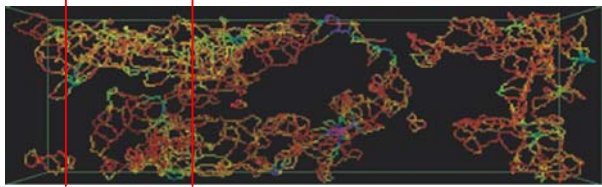
LOI: Ignition loss (1,000°C), NSS: Could not be analyzed due to insufficient samples

Analyzed by ALS Chemex Ltd., Canada

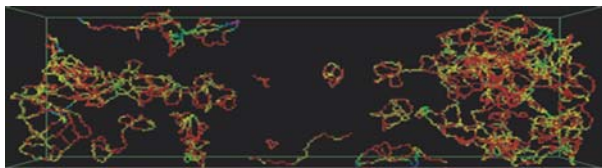
Concrete pavement after one year (thickness : 30cm)



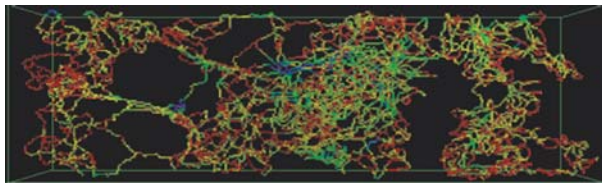
No.0 8.12%,1.44mm



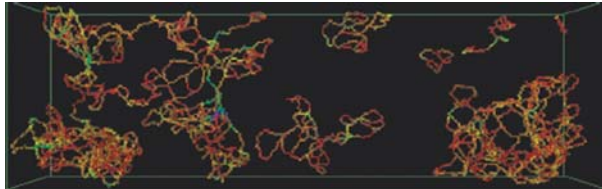
No.1 **22.5%**,1.2mm



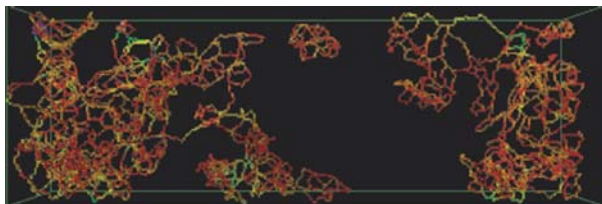
No.2 14.2%,1.2mm



No.3 **26.6%**,1.2mm



No.5 16.1%, 1.2mm

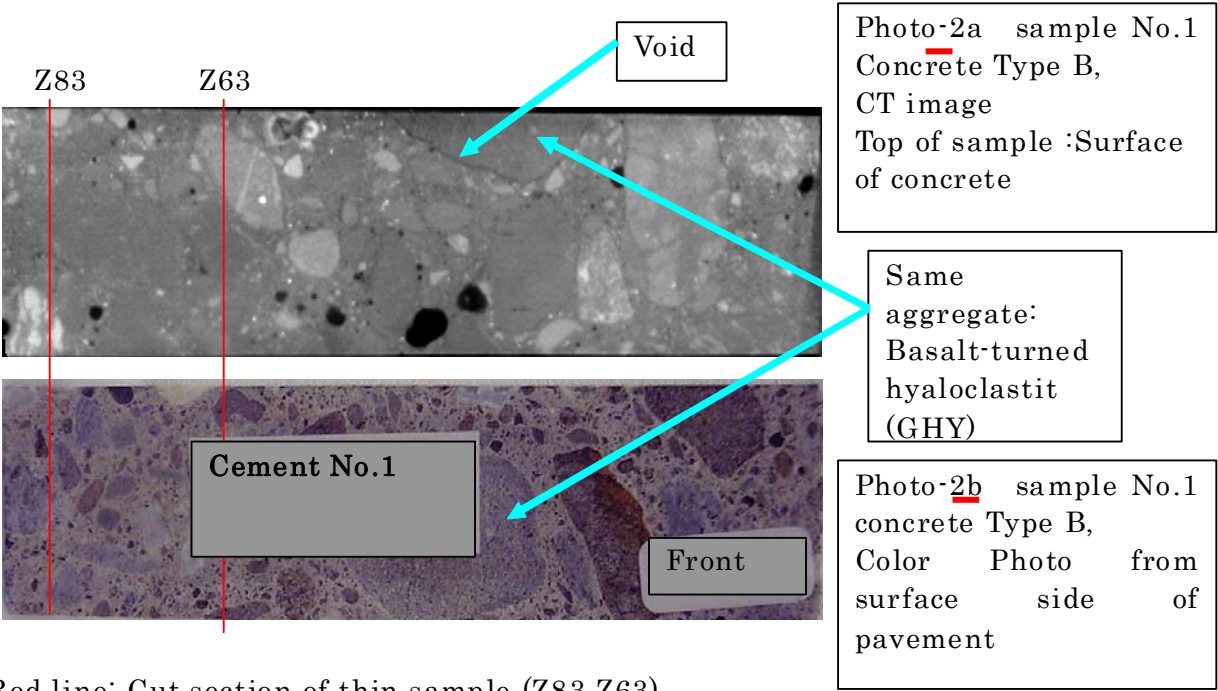


No.8 15.4%,1.2mm

Photo 1 Cross sections of six concrete samples (Type B, all samples are the same size :2.5 x 2.5 x 10 cm) obtained by CT scanner **and** three-dimensional void analysis (%;;void ratio, mm: maximum crack width)

(No.0: First layer (0 to 2.5 cm from top surface), No.1: Second layer (2.5-5 cm from top surface), No.2: Third layer (5-7.5 cm from top surface), No.3: Forth layer (7.5-10 cm from top surface), No5: Sixth layer (12.5-15 cm from top surface), No.8: Ninth layer (20-22.5 cm from top surface))

Red line: Cut section of thin sample (Z83, Z63)



Red line: Cut section of thin sample (Z83,Z63)

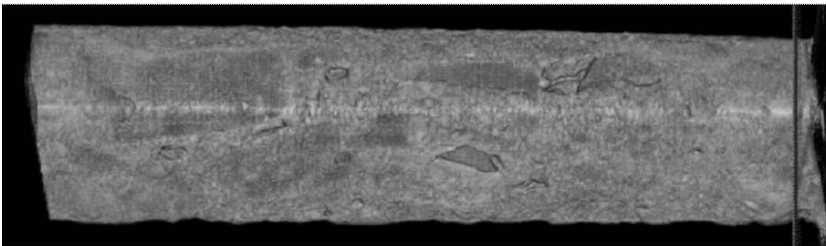


Photo-3a sample No.0
concrete Type B,
top of sample: surface
of concrete pavement,
Rotation of 45 degrees

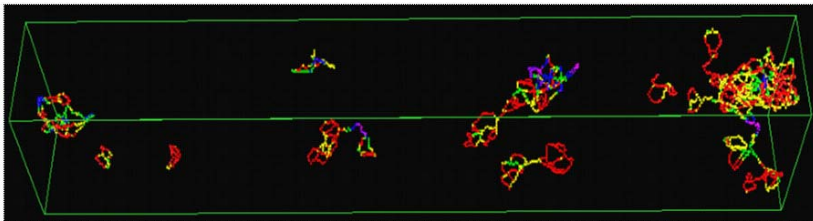


Photo-3b sample No.0
concrete Type B,
Upper side of sample:
surface of concrete
pavement,
Three dimensional
crack analysis by CT

Same aggregate with white
rim,
Basalt-turned hyaloclastit
(GHY)

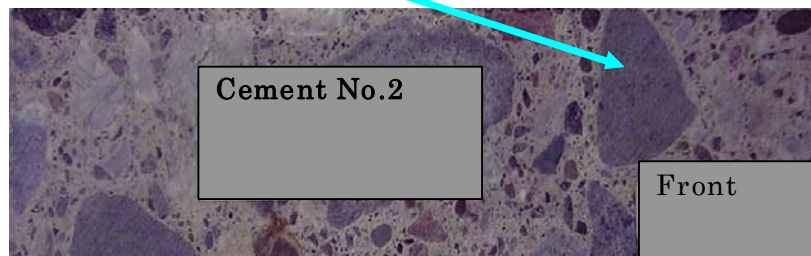
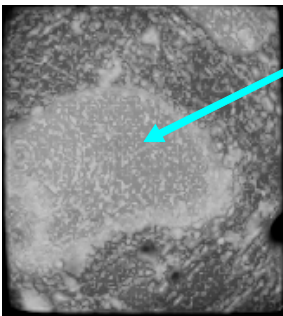


Photo 4a

Sample: No.2, Z-17*

White rim around aggregate

Photo 4b

Sample: No.2

Top of sample: surface of concrete pavement

*Z-17 means the section of 15.3mm apart from the right end of sample No.2

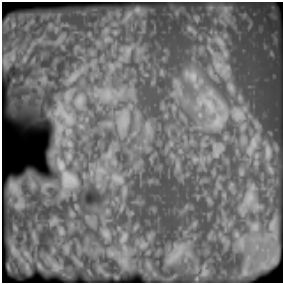


Photo 5 Sample:No0, Z-26*

Cirrocumuli-like patterns appearing
all over aggregate

Aggregate: Basalt-turned hyaloclastite
(GHY)

*Z-26 means the section of 23.4mm apart from the right end of sample No.0

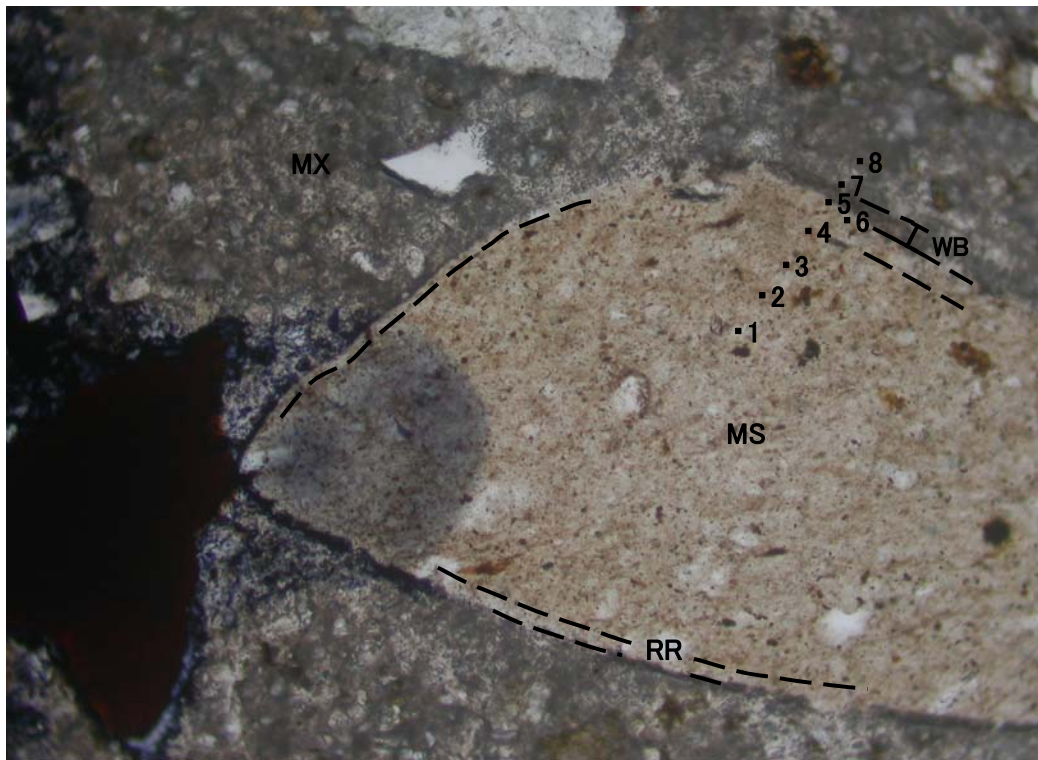


Photo 6 The points measured by EPMA—measurement points on the mudstone(MS)
 Sample:No2 Z62 RR: Rim of reaction
 WB: white reaction zone of cement mortar

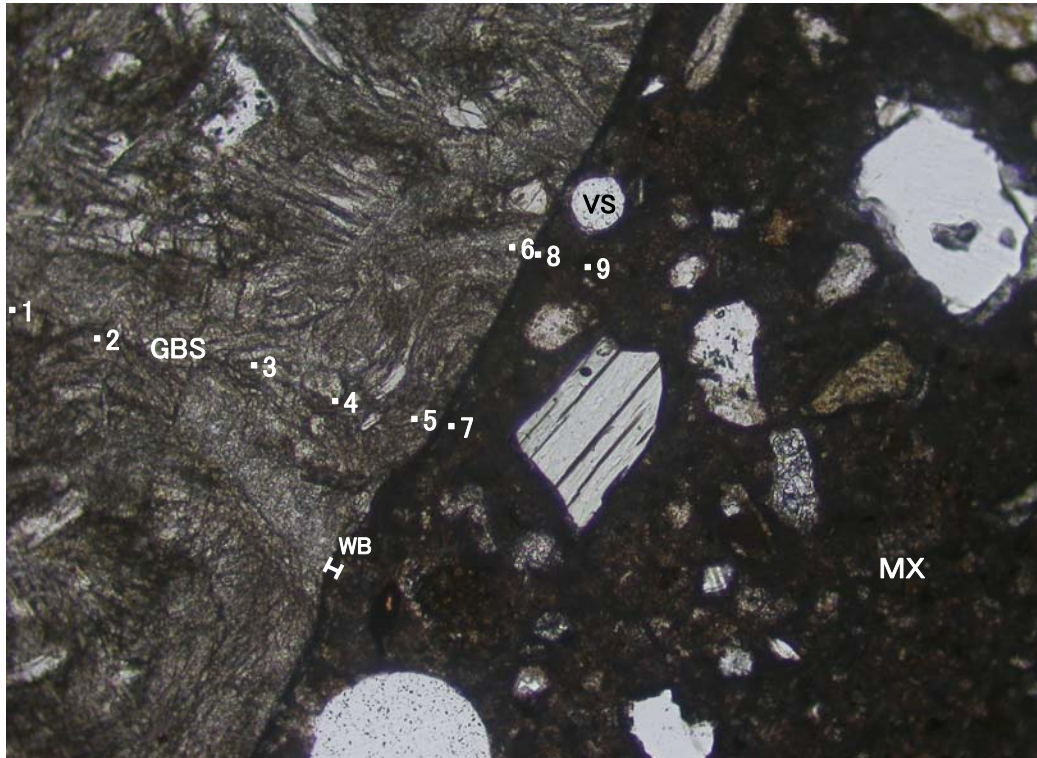


Photo 7 The points measured by EPMA—measurement points on the basalt-turned greenstone(GBS)
 Sample:No2 Z62 VS: Air void
 WB: white reaction zone of cement mortar

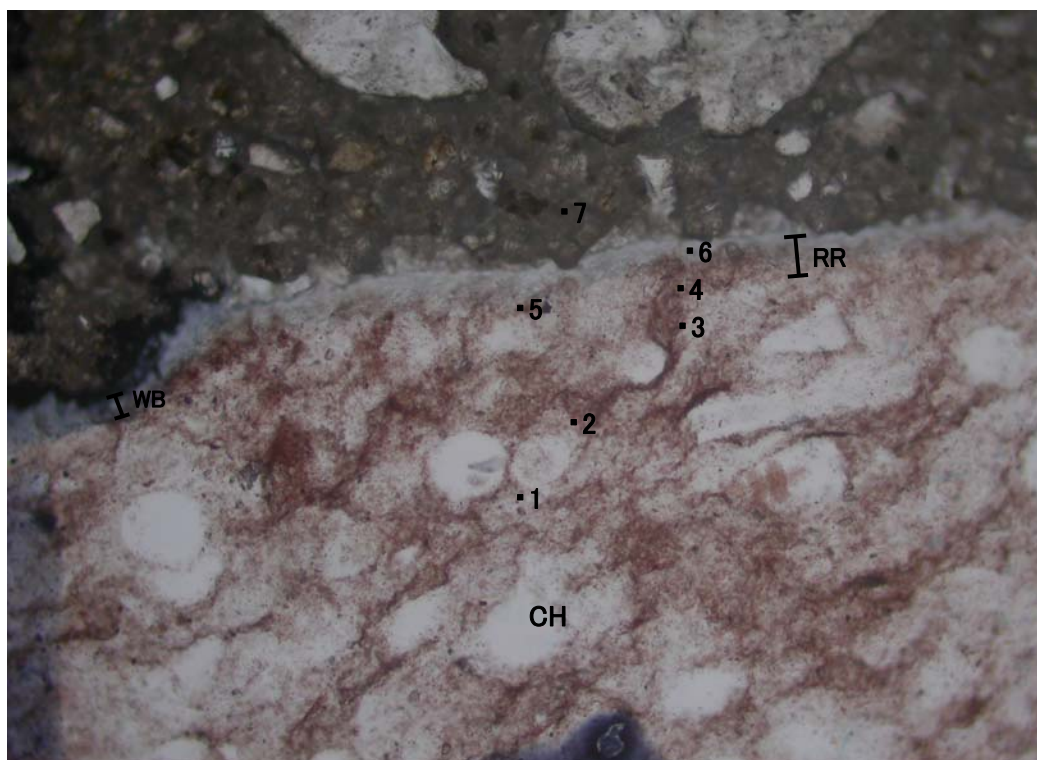


Photo 8 The points measured by EPMA-measurement points on the chert(CH)
 Sample:No2 Z62 RR: Rim of reaction
 WB: white reaction zone of cement mortar

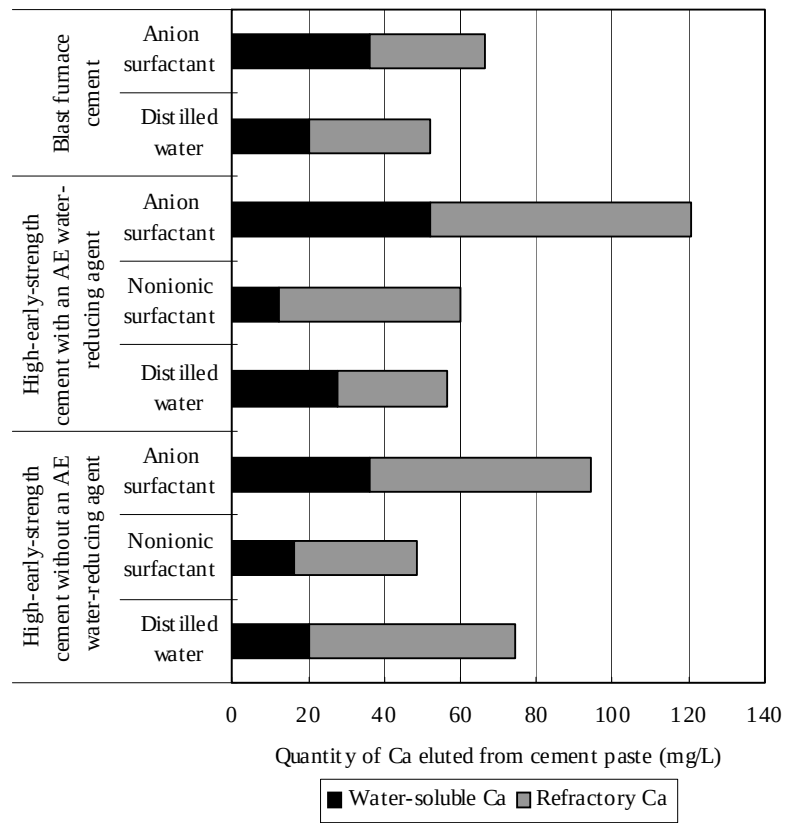


Figure 1 The quantity of water soluble calcium and refractory calcium of cement paste in various solutions

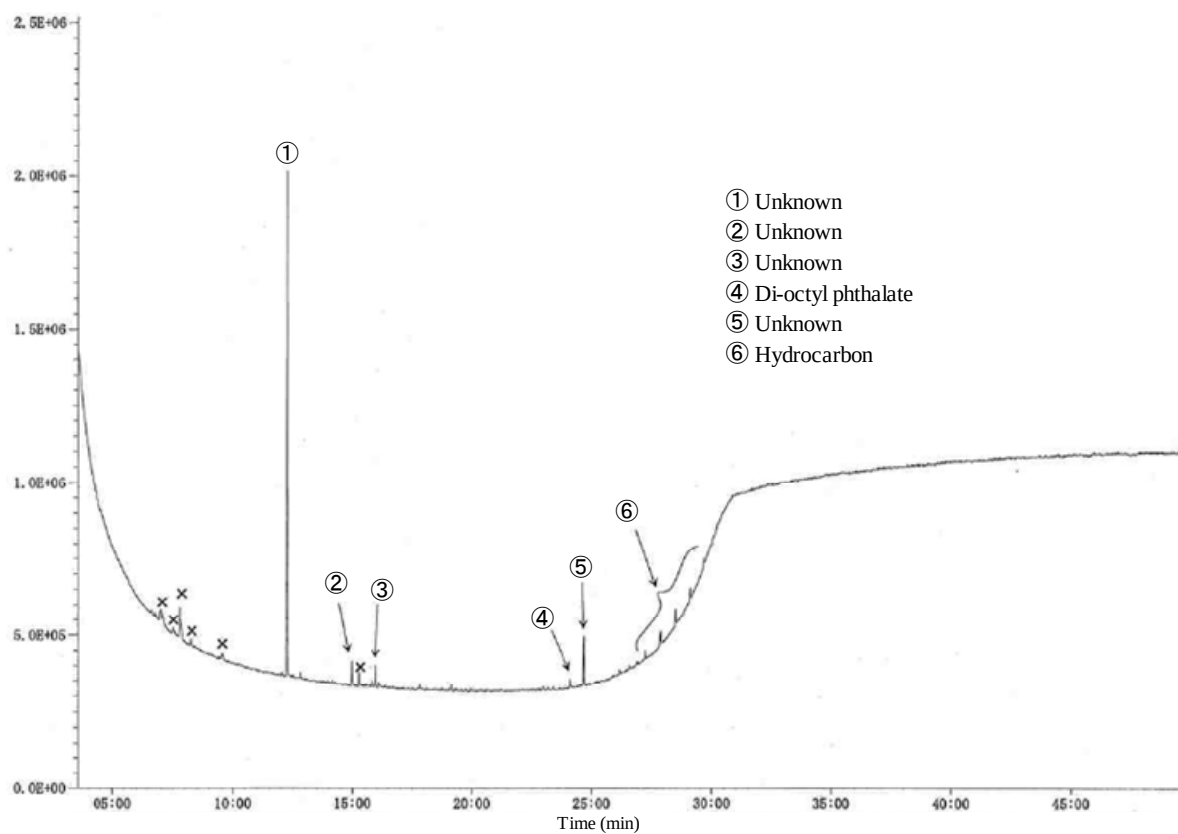


Figure 2 GC-MS spectrum for Mortar powder for concrete Type B

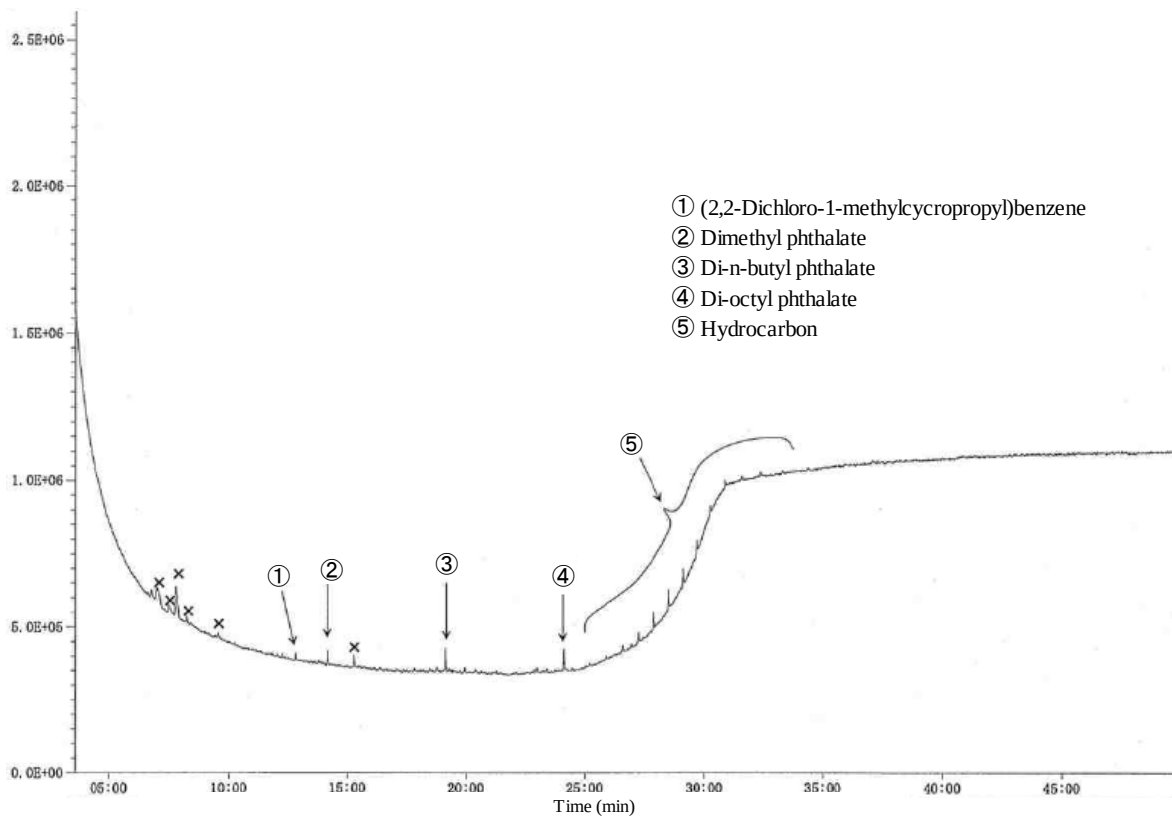


Figure 3 GC-MS spectrum for aggregate powder for concrete Type B

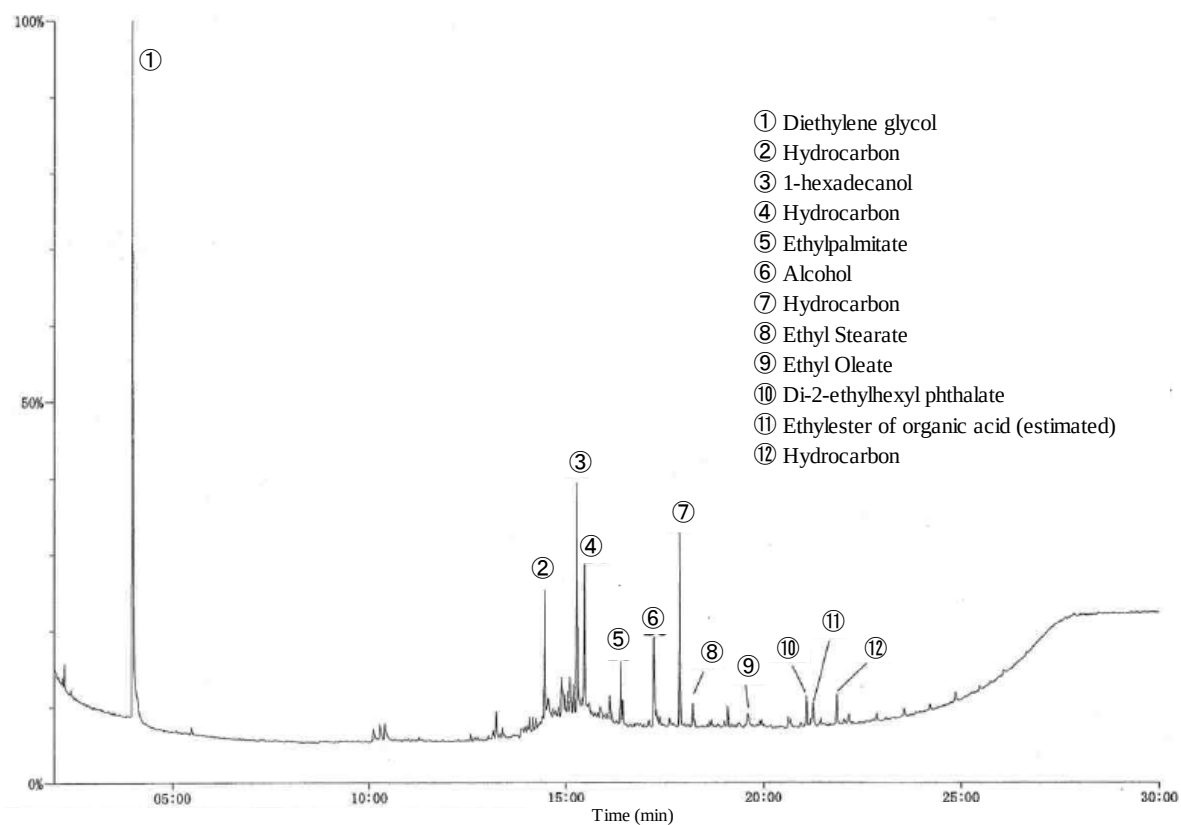


Figure 4 GC-MS spectrum for new-paste powder with AE water-reducing agent

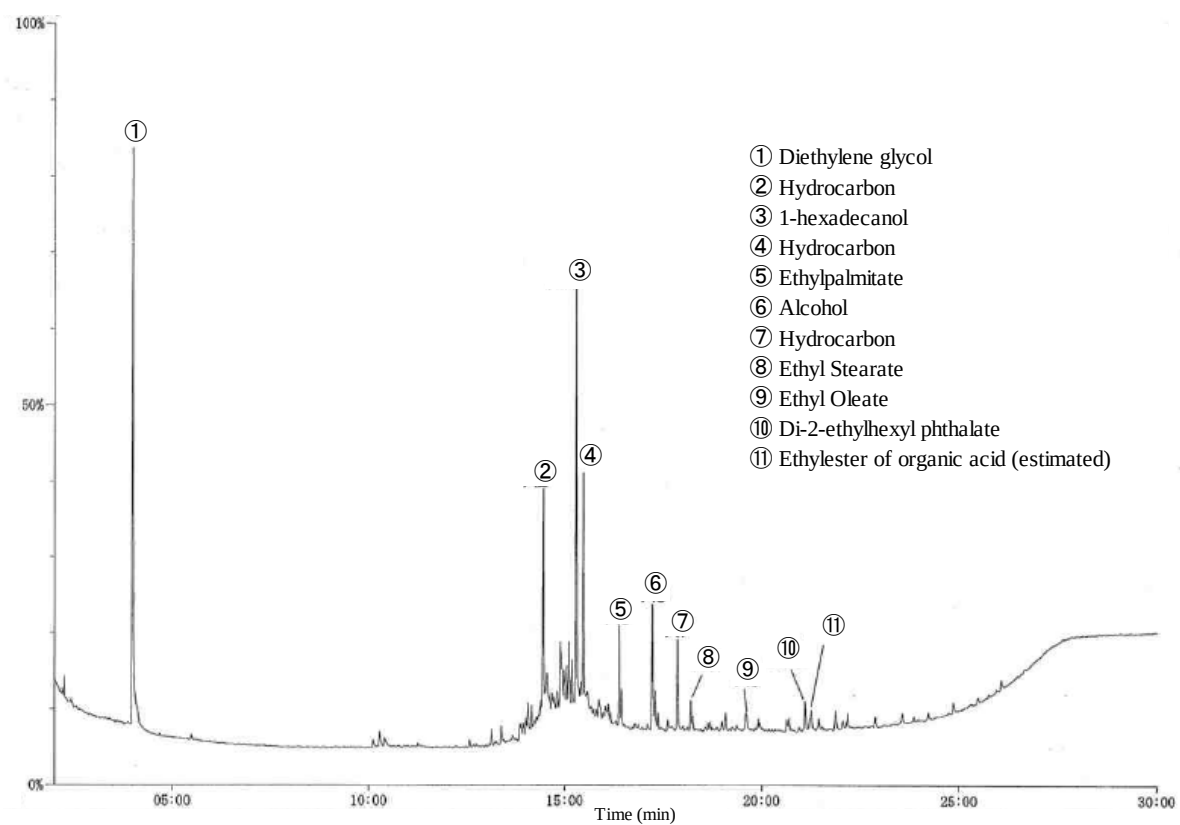


Figure 5 GC-MS spectrum for new-paste powder without AE water-reducing agent

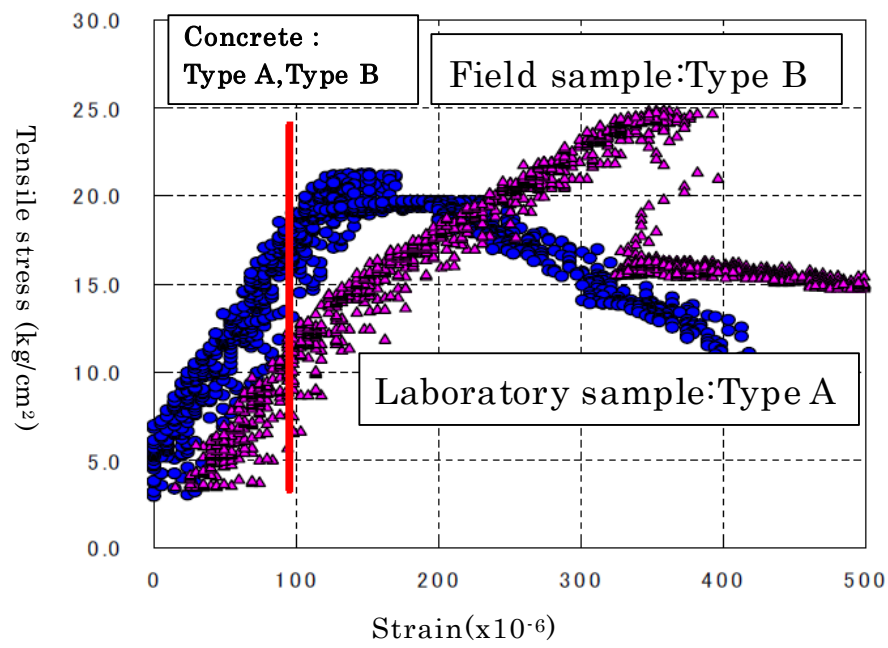


Figure 6 Results of tensile test for the samples taken from concrete pavement

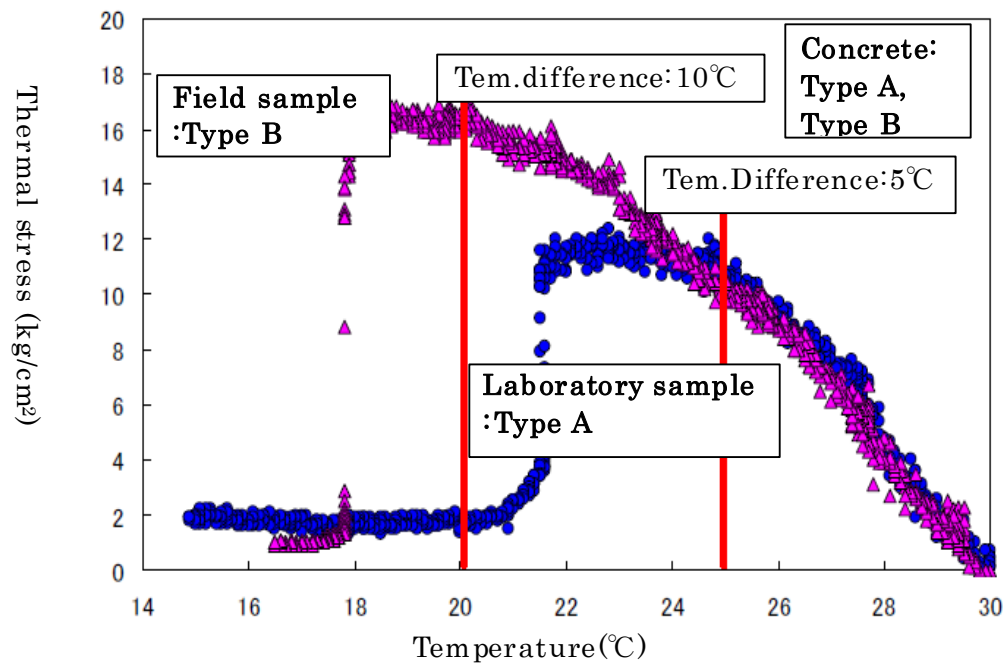


Figure 7 Results of thermal-stress test for the cement concrete

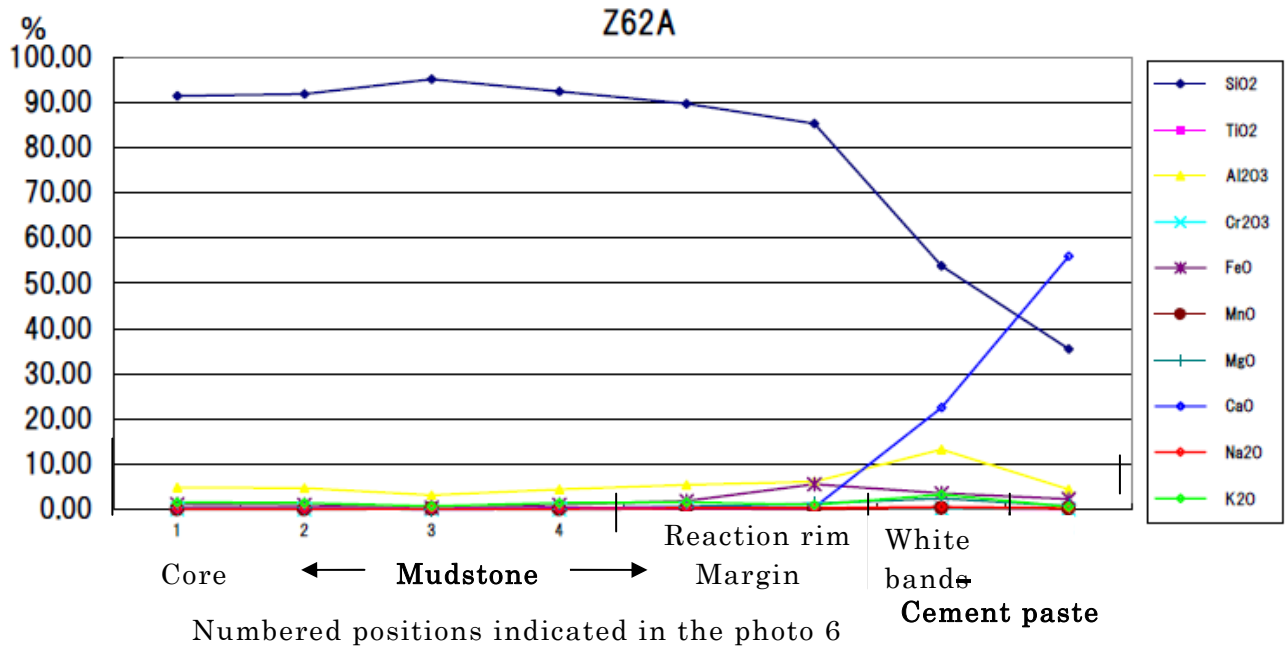


Figure 8 The points measured by EPMA in the Mudstone in Photo 6 (Z62A) in concrete type B; No.5& 6: reaction rim; No.7:white bands in the cement; No.7 & 8: cement paste. Numbers in the horizontal axis refer to the numbered position indicated in Photo 6

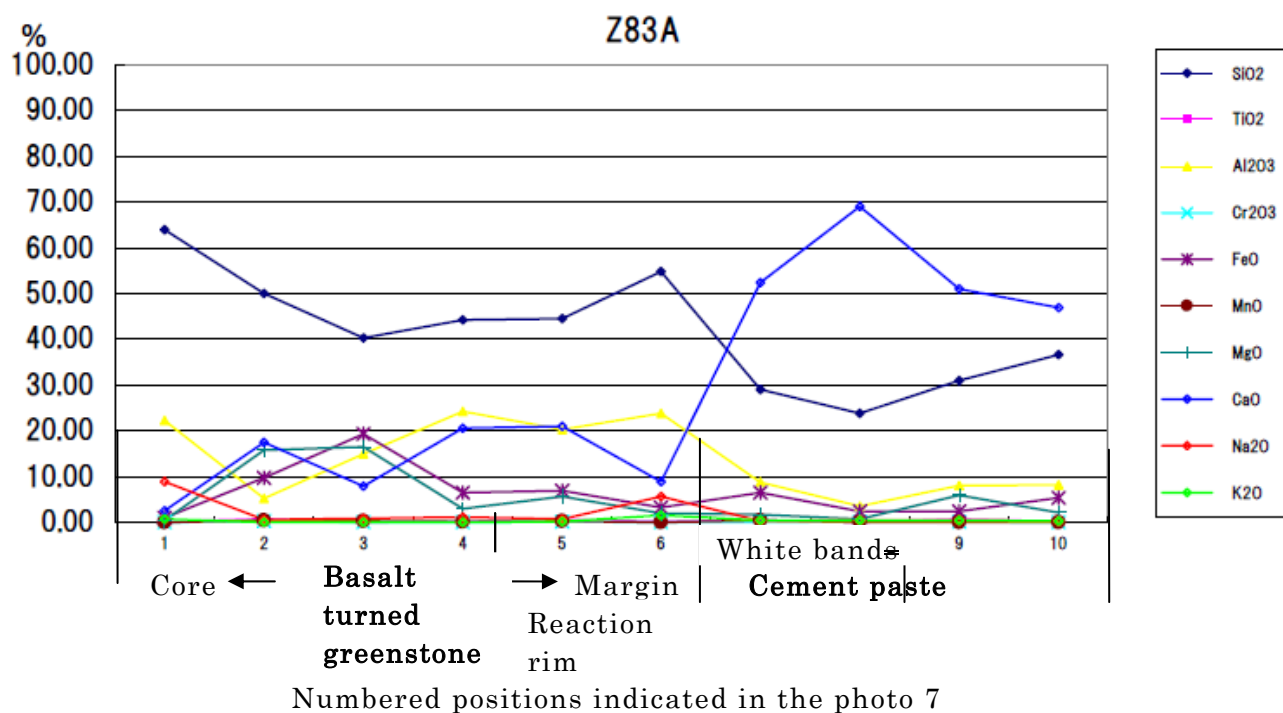


Figure 9 The points measured by EPMA in the Basalt turned greenstone(Z83A) in Photo 7 in concrete type B; No.5 & 6 the reaction rim; No.7 & 8 white bands in the cement; No.9 & 10 cement paste. Numbers in the horizontal axis refer to the numbered positions indicated in photo 7.

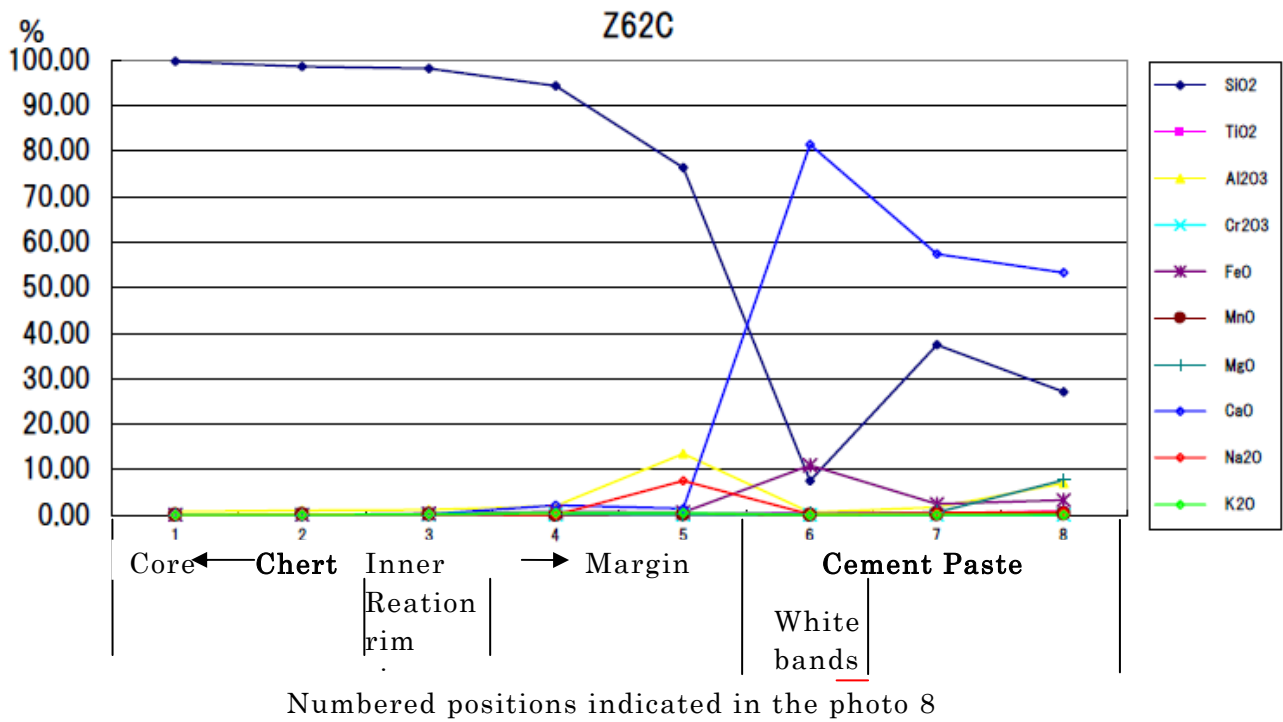


Figure 10 The points measured by EPMA in the Chert in Photo 8 (Z62C) in concrete type B; No.3: inner reaction rim; No.6:white bands in the cement; No.6, 7& 8: cement paste, Numbers in the horizontal axis refer to the numbered positions indicated in photo 8.