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Decalcification of Cement Concrete Structures and Dissolution of Bitumen by Windshield Washer Fluid

Akihiro MORIYOSHI[†1]*, Masayoshi TABATA[†2], Hiromitsu KITAGAWA[†3], Katsuya TOKUMITSU[†4], and Noboru SAEKI[†1]

[†1] Dept. of Civil Engineering, Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo 060-8628, JAPAN
[†2] Dept. of Molecular Chemistry, Graduate School of Engineering, Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo 060-8628, JAPAN
[†3] Formerly Dept. of Civil Engineering, Graduate School of Engineering, Faculty of Engineering, Hokkaido University, N13W8, Kita-ku, Sapporo 060-8628, JAPAN
[†4] Technical Research Laboratory, The Nippon Road Co., Ltd., Tamagawa 2-11-20, Ota-ku, Tokyo 146-0095, JAPAN

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A new phenomenon of decalcification of the cement concrete structure and dissolution of bitumen in bituminous pavement is described, caused by the surfactants included in the windshield washer fluid of automobiles. Decalcification occurs in cement concrete samples in the laboratory even at low concentrations of surfactant of 25 ppm. Recently, foam with fine bubbles have been observed in the water on pavement just after rain worldwide. The decalcification reaction was identified as an ion exchange reaction between the calcium ions Ca^{2+} in the concrete and Na^{+} in the surfactants using the electron spectroscopy for chemical analysis (ESCA) method. Bitumen was also found in the decalcified cement concrete, from which the Ca component had dissolved out gradually with time.

Keywords
Cement concrete, Decalcification, Surfactant, Windshield washer fluid, Ion exchange, Bitumen

1. Introduction

Recently, foam can be increasingly seen on wet street surfaces just behind the tires of moving car traffic, especially soon after it has begun to rain. The foam is white, whereas the water is black, and composed of many fine bubbles. Some of authors have observed this phenomenon in Belgium, Canada, Germany, France, Italy, Japan, the Netherlands, South Africa, Sweden, the United States, and other countries. This foam was previously ascribed to the aqueous surfactants used in the windshield washer fluid (WWF, content of surfactant: 0.5%[1]) of automobiles[2]. The same types of WWF are used around the world.

Recently, we found that these surfactants can not only dissolve the bitumen in bituminous pavements but can also decalcificy (carbonize) cement concrete structures such as slabs, piers of bridges, and various concrete structures near roads through a cation exchange reaction, *i.e.*, the Ca^{2+} which of the major components (CaO and /or $Ca(OH)_2$) in the cement can quickly be replaced by the Na^{+} of the surfactant components such as sodium alkylbenzene sulfate (SABS) and/or sodium polyoxyethylene nonylphenyl ether sulfate (SPNES) reagent, leading to cracking, spalling and disaggregation. Here, we report that the deterioration of the bitumen as well as the cement concrete structures is induced by the surfactants and characterize the deterioration of the bituminous pavements and concrete structures using the ^1H nuclear magnetic resonance (NMR) and electron spectroscopy for chemical analysis (ESCA) methods.

2. Experimental

Several samples were collected and tested to estimate the degree of deterioration by the surfactants as shown in **Table 1**, together with the environmental and traffic conditions. The Pier (P1) and Pier (P2) samples were taken from the piers of a road and railway, respectively, and Building (Bu) in a city burdened with heavy car traffic was taken from the wall of a building which was destroyed by an earthquake.

The concrete samples for the test were prepared as follows: Five concrete samples (Slab (S1), Slab (S2), Pier (P1), Pier (P2), and Building (Bu)) were milled to fine sand (under 0.074 mm). The concrete and soil

* To whom correspondence should be addressed.
* E-mail: moriyosi@eng.hokudai.ac.jp

Table 1 Environmental and Traffic Conditions at the Sampling Sites

Sample[a]	Ave. annual temp. [°C]	Crack length [cm]	Amount of rainfall [mm/year]	Traffic volume [vehicles/day]	Decalcification depth [cm]	Service [years]	Ground height [m]	Weight ratio [%]
Slab (S1)[b]	16.0	100-300	1690	160000	3.0	23		0.001
Slab (S2)[c]	14.9	100-200	1575	32000	3.1	33		0.004
Pier (P1)[d]	12.1	5-10	1385	53000	2.3	—	1.5	0.002
Pier (P2)[e]	12.1	5-10	1385	25000	2.2	31	2.0	0.03
Building (Bu)	12.1		1385	79000	—	26	3.5	0.5
Soil (So)	12.1		1385	79000		26		1.4

a) RMS diameter of less than 0.074 mm. b), c) Slab thickness of cement concrete, 21 cm. d), e) Piers of overhead bridges along road.

samples weighing 2.45-0.1 N (245-10 g), were then extracted with methanol to obtain the bitumen and surfactant contents using a glass Soxhlet apparatus for 24 h. Chloroform was then used to re-extract the organic lipophilic materials from these samples. The weight ratio (%) of the extracted material (bitumen including surfactants) to original sample weight (milled fine sand) are also shown in **Table 1**.

The extent of decalcification, *i.e.*, the depth of carbonization, in the cement concrete samples in **Table 1** was measured by the phenolphthalein method[3]. ^{1}H NMR spectra were recorded on a JOEL EX 400 using $CDCl_3$ solution with tetramethylsilane (TMS) as a standard signal at 23.7°C. ESCA spectra were recorded on a VG Scientific ESCALAB Mk2. The stripping test (JPI-5S-27-86) for specimen covered straight bitumen (penetration: 80/100) was performed using various surfactant solutions of 0.5% concentration.

3. Results and Discussion

Table 1 shows the degree of deterioration by decalcification in various concrete samples and soil under various environmental and traffic conditions. **Table 1** suggests that the Soil (So) was the most impregnated and deteriorated material (by weight ratio) contaminated with surfactant associated bitumen materials, and the five concrete samples also contained a large amount of the surfactants associated with bituminous materials (standard content of bitumen in bituminous pavement: 6%) contrary to our expectation. Content of organic contamination (weight ratio) depended upon the porosity of the concrete (cement concrete of buildings has high porosity[4], because of the high content of water/cement), traffic volumes, and service lives. In fact, we found these concrete samples being white, suggesting that so-called progressive carbonization had occurred. Therefore, a wide angle X-ray analysis was performed to identify the mechanism for the deterioration of the white samples. However, we failed to detect the typical peak of the cristobalite formed by the so-called alkali silica reaction at $2\theta = 21.9$°C, usually considered as the carbonization product[5]. Therefore, no alkali silica reaction had occurred in these samples, irrespective of the white appearance. Therefore, we concluded that the severe spalling, cracks, and disaggregations were created by the effect of prolonged exposure to surfactants.

3. 1. NMR

^{1}H spectra of the samples were analyzed to determine the components of the deteriorated materials. The spectra are shown in **Fig. 1** using $CDCl_3$ solution of (a) Slab (S1) sample and (c) the original bitumen sample used. This spectrum is similar to those of the other cement concrete samples and soil. The peaks at 0.9, 1.2, and 1.5 ppm were assigned to the alkyl protons of the CH_3, CH_2, and CH moieties in the bitumen, respectively. The peaks at around 3.5-4.4 ppm were assigned to the oxyethylene moiety, $-(O-CH_2CH_2)_n-$, in the (b) SPNES sample, a part of which is shown as (b)[6]. The peaks at *ca.* 6.7-7.8 ppm may be assigned to the phenyl group protons in the SABS and/or SPNES surfactant[7]. These results naturally suggested that bitumen and surfactants are included in the deteriorated materials. The peaks at *ca.* 5.1-5.5 ppm were assigned to the material used to paint white lines on bituminous pavement and diesel exhaust particulate (DEP). The anionic surfactants were never observed in newly constructed bituminous pavements and concrete structures. Therefore, the ^{1}H NMR method can appropriately apply to detect bitumen and surfactant intrusions in concrete.

3. 2. Deterioration

Immersion tests were performed to examine the effects of surfactants on cement concrete (**Table 2**) using aqueous solutions with various surfactant contents (5000-25 ppm at 20°C), typical of WWF. Immersion of a cement concrete block ($2.5 \times 2.5 \times 5$ cm) into solutions of surfactant (sodium laurate acid (SLA): 20 ppm) caused the solution (300 m*l*) to turn a muddy color and the content of calcium ions became about 5 ppm after 7 days, and white substances were deposited on the concrete.

Weight loss in a aqueous solution (500 ppm) of SLA was around 0.17% after 8 h at 20°C. The white substances (powder) were physically collected from the

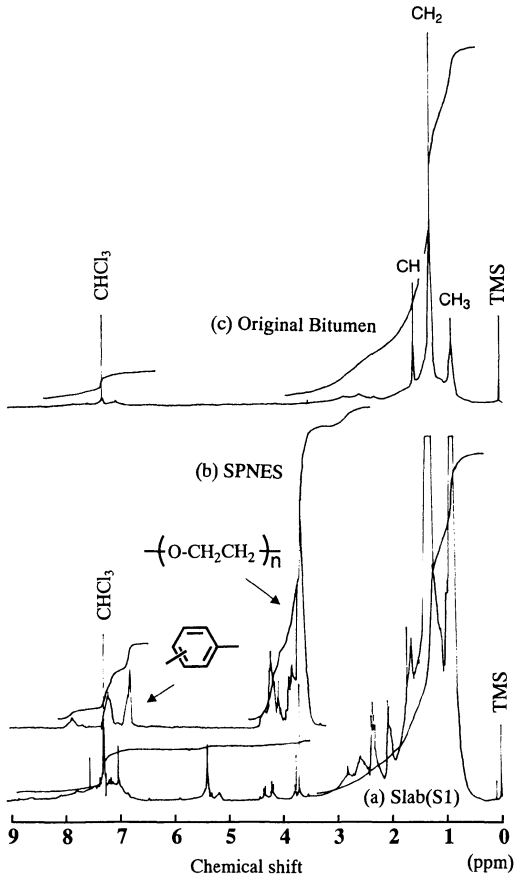

Fig. 1 ^{1}H NMR (400 MHz) Spectra of Samples, (a) Slab (S1), (b) SPNES Surfactant, and (c) Original Bitumen Observed with Tetramethylsilane (TMS) as a Standard at 23.7°C

Table 2 Composition of Cement Concrete Sample Made in the Laboratory

Water/cement: 45%
Sand/aggregate: 42%
Max aggregate: 15 mm
Slump: 8 cm
Portland cement
Air content: 4.5%
Water reducer: 2.5% by weight of cement
Air entraining agent: 1.25% by weight of cement

This composition is identical to that of the disaggregated cement concrete bridge deck.

surface of the specimen and dried at 40-50°C for 24 h.

In general, the maximum dissolution effect for cement concrete occurred at 200 ppm for every surfactant. Content of Ca^{2+} in aqueous solutions (300 m*l*) with various surfactant contents by immersing cement concrete blocks ($2.5 \times 2.5 \times 5$ cm) was a maximum (1.65-2.05 ppm) at 1 day for maximum dissolution solutions, although the Ca^{2+} in the solution chemically reacted with the surfactants. In contrast, distilled

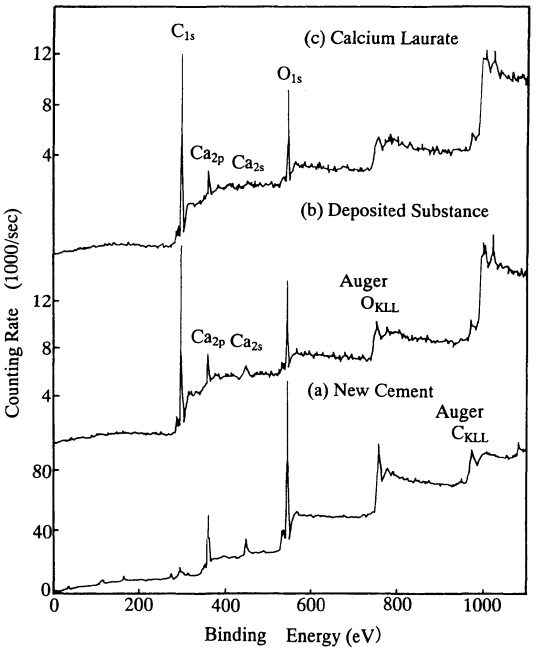

Fig. 2 ESCA Spectra of Materials, (a) New Cement, (b) Deposit of White Substance on the Cement Concrete Block ($2.5 \times 2.5 \times 5$ cm) Immersed in the Aqueous Solution of SLA (1000 ppm, 20°C, 8 h), and (c) Calcium Laurate

water in the same method tends to dissolve a maximum of 0.95 ppm at one day.

Straight bitumen was also easily dissolved by various 0.5% surfactant solutions in the stripping test, in which 60-80% or more of covered bitumen was stripped out and the solutions all became black. The stripping ratio was only 5% for distilled water.

The same black organic matter was identified using ^{1}H NMR in water with fine bubbles collected from bituminous pavement and in decalcified cement concrete structures. The content of surfactant in the water was 30 ppm or more just after rain as measured by liquid chromatography.

3. 3. ESCA

Electron spectroscopy for chemical analysis (ESCA) was carried out to determine the types of metal ions incorporated in the white deposit powder together with the new cement and SLA as standards. The results showed that the ion exchange reaction for Ca^{2+} and Na^+ components had occurred[8]. **Figure 2** shows the ESCA spectra of (a) new cement concrete, (b) deposits obtained after 8 h immersion of the new cement concrete in the solution of SLA (1000 ppm), and (c) calcium laurate, respectively. The spectrum of the (b) white deposit is almost the same as that of (c) calcium laurate, because the ratio ($Ca_{2p}/Ca_{2s} = 3.7$) of the two peak intensities of Ca_{2p} and Ca_{2s} is identical to calcium laurate. In contrast, Na_{1s} (1071 eV) observed in the

new concrete cement was not detected in this white deposit, although strong peaks due to C_{1S} and C_{KKL} in surfactants were clearly noticed in the deposit at the same time. Moreover, calcium ion peaks of Ca_{2p} (347 eV) and Ca_{2s} 447 eV in (b) decreased from 52 (counting rate, $\times 1000\ sec^{-1}$) to 7.7 (counting rate, $\times 1000\ sec^{-1}$), and from 35.3 (counting rate, $\times 1000\ sec^{-1}$) to 6.4 (counting rate, $\times 1000\ sec^{-1}$), respectively.

These observations strongly indicate that the white deposit is not cement concrete but calcium laurate[9]. Therefore, when cement concrete is immersed in surfactant solution, an ion exchange reaction between the Ca^{2+} in the cement concrete and the Na^+ in the anion type surfactant occurs.

Such a cation exchange reaction and dissolution of bitumen have not been reported. Therefore, based on the experimental observations, we propose a new cation exchange reaction shown below. These reactions show that the Ca component in the C–S–H (xCaO·ySiO$_2$·zH$_2$O, $x/y = 1.2$-2.0, $z/y \simeq 1.5$) and/or calcium hydroxide as the major components in the cement, is replaced by the Na component of the surfactants through ion exchange in water solution[10].

3. 4. Decalcification

Reaction between C–S–H and SLA:

$$3CaO \cdot 2SiO_2 \cdot 3H_2O + 6(R \cdot SO_3Na) \rightleftharpoons 3(R \cdot SO_3)_2Ca + 3Na_2O + 2SiO_2 + 3H_2O \quad (1)$$

Exchange reaction between Ca^{2+} in the concrete and Na^+ in the SLA.

$$Ca(OH)_2 + 2R \cdot SO_3Na \rightleftharpoons (R \cdot SO_3)_2Ca + 2NaOH \quad (2)$$

where R indicates the n-$C_{12}H_{25}$ group.

4. Conclusions

Bitumen in the bituminous pavements is dissolved by surfactants such as SABS and/or SPNES used in WWF and significant decalcification of concrete structures is also induced through the cation exchange reaction between Ca^{2+} in the cement concrete and Na^+ in the sodium surfactants. The reaction leads to both decreased calcium component in the cement concrete and severe deterioration of the concrete structures.

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要　旨

ウインドーウォッシャー液によるセメントコンクリート構造物の脱カルシウム化とアスファルトの溶出

森吉　昭博[†1)]，田畑　昌祥[†2)]，北川　弘光[†3)]，徳光　克也[†4)]，佐伯　昇[†1)]

[†1)] 北海道大学大学院工学研究科土木工学専攻，060-8628 札幌市北区北 13 条西 8 丁目

[†2)] 北海道大学大学院工学研究科分子化学専攻，060-8628 札幌市北区北 13 条西 8 丁目

[†3)] 元北海道大学大学院工学研究科土木工学専攻，060-8628 札幌市北区北 13 条西 8 丁目

[†4)] 日本道路(株)技術研究所，146-0095 東京都大田区多摩川 2-11-20

アスファルト舗装で雨の降り始めに見られる表面水の細かい泡はウインドーウォッシャー液中の界面活性剤が主な原因であり，この泡は日本だけでなく世界中で観測されている。本論文は，自動車用のウインドーウォッシャー液中の界面活性剤が 25 ppm の低濃度でもセメントコンクリート構造物中のセメントの脱カルシウム化をもたらすことを道路沿いの種々のセメントコンクリート構造物，および実験室の作製供試体の浸漬実験や ESCA 法等から最初に明らかにした。すなわち，本研究は陰イオン系の界面活性剤を有するウインドーウォッシャー液中の Na^+ 等がセメント中の Ca^{2+} と急速に化学反応し，セメントの主要鉱物である Ca 成分が次第に外部に溶け出すこと，また戸外で採取した脱カルシウム化したセメントコンクリート構造物には界面活性剤とアスファルトが内部に蓄積されていることを見い出した。