

Control of crystal polymorphism of CaCO₃ generated by self-healing under controlled temperature and pH

*Risa Sengoku¹⁾, Heesup Choi²⁾ and Masumi Inoue³⁾

^{1), 2), 3)} *Department of Civil and Environmental Engineering, Kitami Institute of Technology, Japan*

¹⁾ 1497.mm@gmail.com

ABSTRACT

Generally, cracks are inherent in reinforced concrete structures and can lead to serious damage during their service period. Repeated occurrence of such damages will lead to the enlargement of the cracks, thereby allowing other deteriorating elements such as CO₂ and Cl⁻ to further penetrate the concrete, and this can have serious consequences for the concrete structure. This study focuses on the type of calcium carbonate (CaCO₃) crystals generated by the self-healing phenomenon. Owing to polymorphism, CaCO₃ has three types of crystal forms—calcite, vaterite, and aragonite—whose formation can be controlled by the temperature and pH. Vaterite is also generated most densely among the polymorphs, and self-healing can be expected. Therefore, an experiment was carried out to establish the conditions required to generate vaterite. A saturated Ca(OH)₂ solution with CO₂ nano-bubbles was used for the effective self-healing. The temperature was set to 20 and 40°C and pH was fixed at 9.0. The results showed that the supply of Ca²⁺ and CO₃²⁻ promoted the reaction of CaCO₃ under the self-healing condition using the saturated Ca(OH)₂ solution that supplied CO₂ micro- or nanobubbles, and it was confirmed that relatively large cracks (>0.1 mm) exhibited self-healing effect effectively only in cementitious material. In addition, the product of the self-healing phenomenon was mostly vaterite for a crystal of CaCO₃ under the condition of pH 9.0 and temperature of 40 °C.

1. INTRODUCTION

Generally, cement-based materials such as the concrete are very important materials that control the quality of a structure. However, concrete is a material whose pulling strength is much less than its compressive strength, and crack outbreaks are unavoidable. It is said that the cracks wider than the permissible crack breadth result in problems with the durability of the structures or the quality of waterproofing in Japan [1].

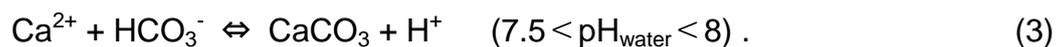
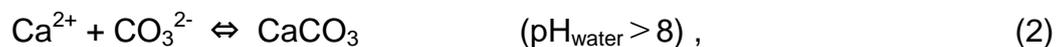
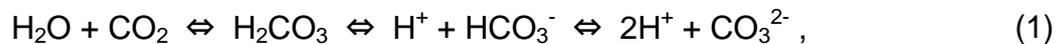
¹⁾ Graduate Student

²⁾ Professor

³⁾ Professor

Deterioration from sources such as Cl^- and the CO_2 penetrate cracks. When such a phenomenon is repeated, it leads to the expansion of the crack width and accelerated deterioration of the concrete, which may finally lead to fatal damage to the concrete structure. Therefore, preventative measures that are appropriate in concrete structures in the early stage of crack outbreak are very important.

On the other hand, in a phenomenon called "self-healing" in which a relatively small crack that was initiated in concrete in an environment with a regular supply of water, water blocks the crack and fills it with a deposit generated by naturally occurring hydration or rehydration reaction [2]. The Ca^{2+} in the concrete react with underwater CO_3^{2-} , and a crystal of CaCO_3 is formed, blocking the crack as a of self-healing mechanism. It was confirmed in earlier studies that cracks narrower than 0.1 mm could close [3]. The following shows below an equation for reactions involved in self-healing.



Choi and others reported that they produced an outer layer on the crack that consisted of a large quantity of CaCO_3 deposits in the self-healing of cement-based materials by letting carbon dioxide flow into the crack as micrometer-sized bubbles based on the above self-healing mechanisms [4]. A crystal of CaCO_3 generally consists of calcite, vaterite, and aragonite. All CaCO_3 , in which $\text{Ca}(\text{OH})_2$ and CO_3^{2-} are coupled, that is generated in cement paste is said to be calcite [5,6]. On the other hand, minute self-healing can be expected as vaterite has a smaller particle size than calcite and is able to fill a cavity [6]. It is reported in past studies that by adjusting the temperature and pH, the form of the CaCO_3 crystal can be controlled [5, 6]. According to the study, crystal polymorphism can be controlled to produce vaterite at a pH of 9.0, aragonite at a pH of 10.5 and calcite at a pH of >11 at normal temperatures [5]. In addition, it is reported that if the temperature is managed when cement is cured in water, calcite is produced at 15–20°C, vaterite is produced at 30–50°C and aragonite is produced at over 80°C [6]. Therefore, it is thought that vaterite may be intentionally generated at a pH of 9.0 and a temperature of 40°C. In this study, therefore, we focused on the CaCO_3 crystal generated by self-healing and investigated better self-healing conditions by adjusting the temperature and pH, and by letting carbon dioxide penetrate fine cracks as nanometer-sized bubbles. By controlling crystal polymorphism so that vaterite is formed intentionally, this could lead to the production of finer self-healing substances. Figure 1 shows the process of the self-healing mechanism explored in this study.

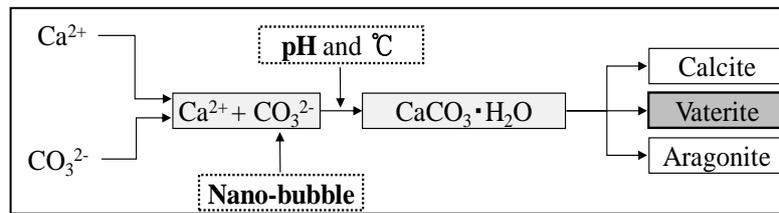


Figure 1. Process of self-healing in concrete.

2. Experiment summary

2.1 Materials

Since the major reaction materials generated during self-healing of cement-based composite materials are controlled by the hydration reaction between cement particles and water [3], multi-faceted performance evaluations of self-healing were conducted with cement paste. The cement-paste sample with water/cement ratio of 40% were produced by using high early strength Portland cement with high early strength (density: 3.14 g/cm³, average particle diameter: 10 μm). The sample was sealed with aluminum adhesive tape right after it was produced. After it was cured at 20 ± 1°C in a thermostatic chamber for 24 h, it was cured in a tank of 20°C water from day 2 day to day 7 day.

2.2 Sample Overview

Figure 2 shows a schematic diagram of the production of a sample and incorporation of cracks in the present study. After the cement paste was dispensed in the mold (dimensions: φ50 × 100 mm) with D6 steel reinforcement (diameter: 6 mm) fixed in the center part, the part with exposed steel reinforcement was sealed with epoxy and subjected to underwater curing for 7 days. After that, the upper and lower parts of the sample were constrained by using a one-axis apparatus, as shown in Fig. 2. Cracks with average widths of about 0.15 mm were incorporated by drying for about 24 h in a drying oven at 105°C, followed by constraining shrinkage of the cement paste to conduct experiments as a sample “before self-healing.” Figure 3 shows the appearance and scale of a crack measuring about 0.15 mm in the sample.

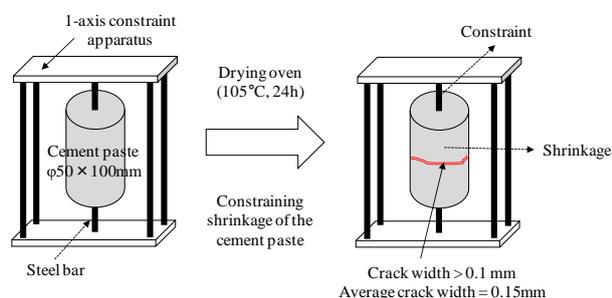


Figure 2. Schematic diagram of fabrication of sample and introduction of cracks.

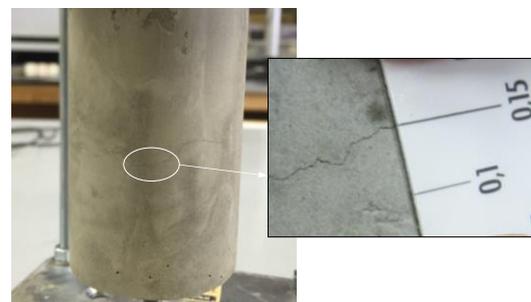


Figure 3. Sample after crack introduction.

2.3 Experimental Method

Table.1 shows experimental factors and experimental conditions. Based on the previous studies, we employed the method of providing micrometer-sized (average particle diameter: 50 μ m) and nanometer-sized (average particle diameter: 50 nm) bubbles that included carbonate ions in a saturated Ca(OH)₂ solution, as self-healing conditions. Moreover, the self-healing conditions was determined by adjusting the temperature to 20°C and 40°C and setting the pH to around 9.0 so that cement hydrates could be controlled to transform calcite into vaterite (Figure 1). The self-healing method proceeded as follows. After CO₂ micro- and nanobubbles were provided for 4 h, a sample was left in a water tank of saturated Ca(OH)₂ solution with added CO₂ micro- and nanobubbles for 20 h. This process counted as 1 cycle (1 day), and we determined that 7 cycles (7 days) was the self-healing period.

Table 1. Experimental factors and conditions.

Sample: Cement paste hardened body (W/C : 40%)		
Self-healing condition	Ca(OH) ₂ + Micro-bubble (CM) Ca(OH) ₂ + Nano-bubble (CN)	pH 9.0
Temperature condition: 20°C (CM-20) , 40°C (CN-40)		
Self-healing period:7 days (7 cycles) (1 cycle:Supply bubble for 4 h + soaking in saturated Ca(OH) ₂ solution for 20 h)		
Crack: Fine cracks due to drying action (105°C, 24 h)		

2.4 Measurement item

Table 2 shows the experimental procedure and content. As Figure 2 shows, we used a sample with introduced cracks, and observed changes in cracked surface as well as the interior in procedure A (right after introducing cracks) and procedure B (after self-healing), using a microscope and an X-ray computer tomography (CT) scan. Meanwhile, Raman spectroscopy analysis was used as the method to evaluate the kinds, as well as the amount of precipitates generated by self-healing. More specifically, we measured the kinds of cracked surface and interiors of self-healing precipitates and the amount of production of calcium hydroxide and calcium carbonate before and after self-healing. Finally, in order to understand how to control the generation of vaterite as the main self-healing precipitate of CaCO₃, we conducted SEM analysis for each case.

Table 2. Experiment procedure and contents.

STEP	Experimental stage	Evaluation	
		Surface and internal section of cracks	Substances precipitated during self-healing
A	Before self-healing	- Microscope - X-ray CT	- Raman spectroscopic analysis - Thermogravimetric–differential thermal analysis (TG–DTA) - SEM analysis
B	After self-healing		

3. Results and Discussion

3.1 Surface Section of the Cracks

Microscope observations were carried out to evaluate the self-healing performance of the cracked surface. Figure 4 shows the observation results of the cracked surface part seen through the microscope. Self-healing precipitates were observed in the surface layer of cracks resulting from self-healing in both CM-20 that supplied nanobubbles and CN-40 that supplied the microbubbles.

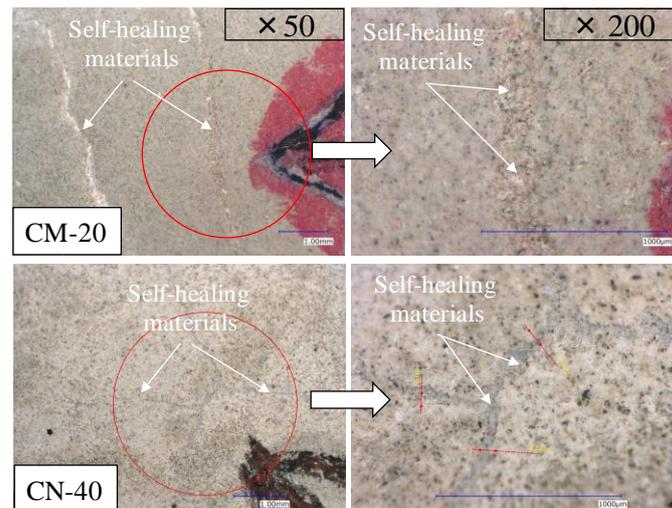


Figure 4. Cracked surface after self-healing.

3.2 Internal Section of the Cracks

In order to figure out how internal cracked parts were blocked by self-healing, an X-ray CT scan was used to observe the internal part of the sample. As an experimental condition, an X-ray (180 kV, 40 μ A) beam irradiated the sample. In addition, as Figure 5 shows, the crack width was calculated by setting an image analysis area of X-ray CT scan and analyzing the 3D image. Figure 6 shows a histogram of the luminance and frequency of the 3D image, and it shows that the boundary in luminance between the void and cement matrix was clearly divided by checking the normal distribution of each peak. After that, assuming that the density of cracks and voids were equal before self-healing, the cubic volume of the void was calculated. By using the difference in density between the precipitates and cracked parts before and after self-healing, the porosity was calculated and compared between samples.

Figure 7 shows the results of void volume of each case before and after self-healing in accordance with the change in temperature of self-healing and supply conditions of carbon dioxide. The void volume was compared after self-healing (B) with the void volume before self-healing (A), which was a standard. As a result, about 30% of void volume under CM-20 decreased from 0.56% to 0.39%, while about 40% of the void volume under CN-40 decreased from 0.47% to 0.28%. As a result of the image analysis with X-ray CT scan, Figure 8 shows cracking conditions at the time of the cracks were introduced and after self-healing. The color of the image changed in accordance with

density. Therefore, the lower the density, the thicker the color, whereas the higher the density, the thinner the color. During the 3D analysis of the images, no clear change of void structure before and after self-healing was identified. It was, therefore, assumed that most of the decrease in void volume, which was presented in Figure 7, was due to the blocking of cracked areas. It was thus concluded that when ultrafine nanobubbles containing CO_3^{2-} ions were supplied with nanoscale Ca^{2+} ions of a saturated $\text{Ca}(\text{OH})_2$ solution at a controlled temperature and pH, the generation and precipitation of self-healing materials was promoted not only on the surface but also inside the crack.

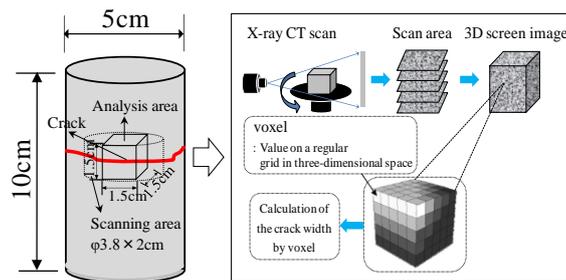


Figure 5. Scanning area and calculation of the crack width [7].

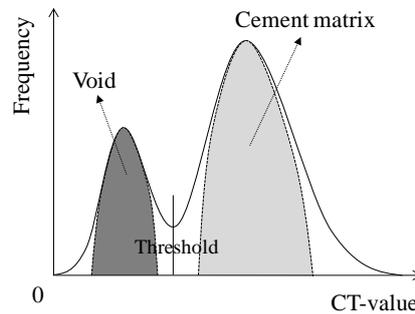


Figure 6. Conceptual diagram of the frequency of CT-values [7].

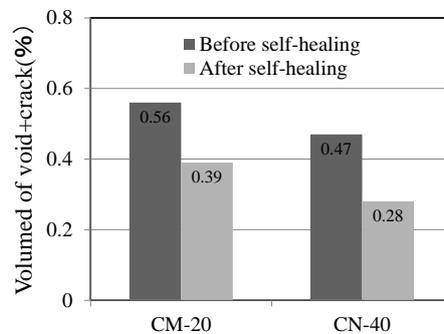


Figure 7. Volume change of (void + crack).

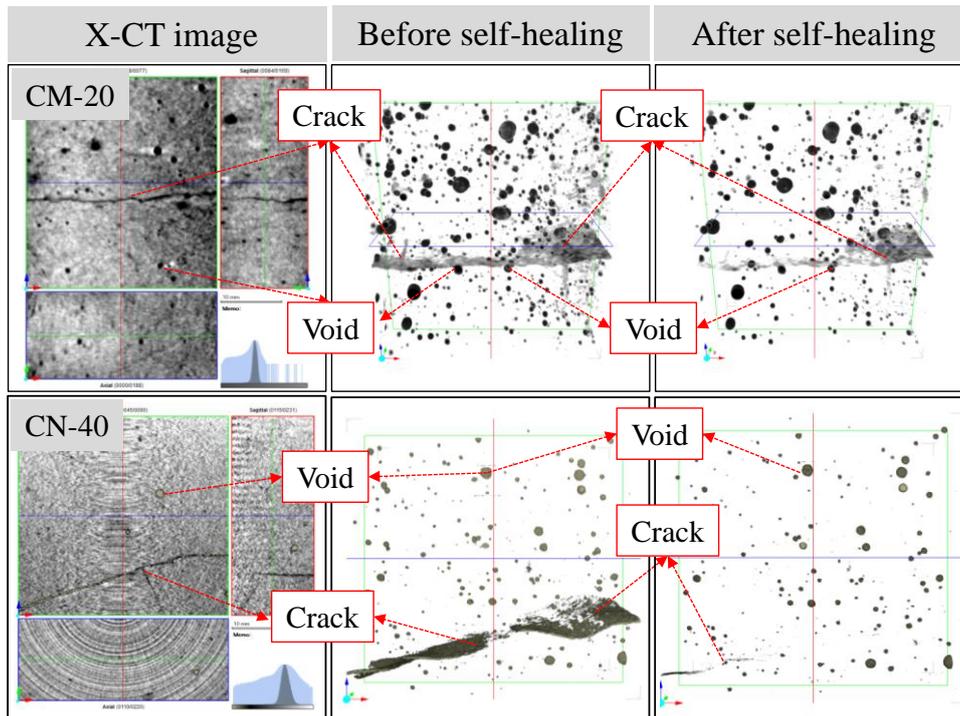


Figure 8. 3D analysis image by Micro X-ray computed tomography.

3.3 Chemical Evaluation of the Precipitated Substances of Self-Healing

3.3.1 Raman spectroscopy analysis

In order to identify crystalline components of precipitates generated by self-healing, it is implemented Raman spectroscopy using a sample obtained from the cracked area, on which a large amount of self-healing precipitates were adhered to (CN-40). Raman spectroscopy is a spectroscopic technique used to analyze molecular level structures from the obtained spectrum by diffracting light (Raman scattered light) that is different from incident light irradiated a sample. A laser was used to irradiate two cracked and non-cracked areas of the sample. Then, by comparing the two peaks of wavelength at the time of irradiation with the peak wavelength of chemical compounds ($\text{Ca}(\text{OH})_2$ and CaCO_3 powder), which were used as the criteria, the chemical compounds of the deposits were identified. Figure 9 shows the result of the measurement. An extremely tiny peak of CaCO_3 powder on the surface of non-crack area was identified at the same position as the peak of CaCO_3 powder. Meanwhile, an obvious peak corresponding to the wavelength of CaCO_3 appeared in the measurement of the cracked part. Moreover, it was confirmed that the peak wavelength in either case did not correspond to that of $\text{Ca}(\text{OH})_2$ powder. It is, therefore, considered that most of the component substance that precipitated after self-healing was CaCO_3 .

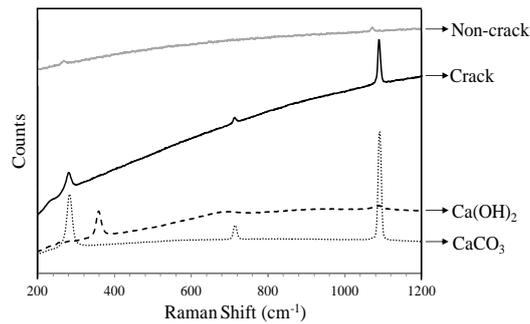


Figure 9. Raman spectroscopy analysis.

3.3.3 Scanning electron microscope (SEM)

Figures 10 and 11 show SEM images of the cracked part and the crack-free part of the sample (CN-40), in which the self-healing temperature was set at 40°C. In the SEM observation, the same sample as the Raman spectroscopic analysis of 3.3.1 was used. Almost no Ca(OH)_2 was observed in the cement solution under the cracked part shown in Fig. 10. However, a large amount of C-S-H gel as well as a number of vaterite, which were adhered to its' surface, were determined. On the other hand, In the non-cracked area in Fig. 11, calcium carbonate (CaCO_3) was hardly observed, and it was confirmed that a large amount of calcium hydroxide (Ca(OH)_2) or C-S-H gel was formed. Therefore, it can be concluded setting the temperature to 40°C and pH to 9.0 and supplying ultra-fine bubbles containing nanometer-sized carbonate ions to the saturated Ca(OH)_2 solution made it possible to produce self-healing precipitates of vaterite, which is expected to contribute to more precise self-healing.

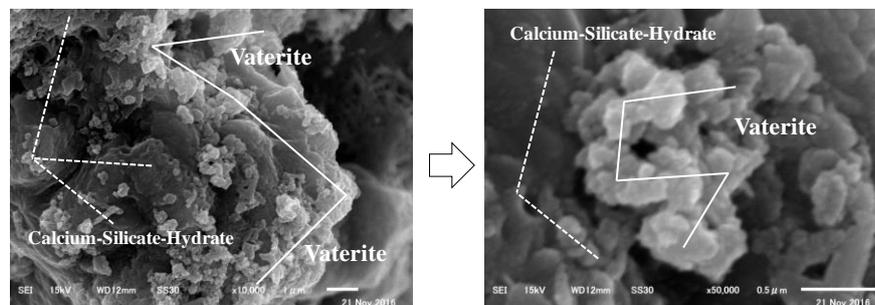


Figure 10. Self-healing materials under cracked part.

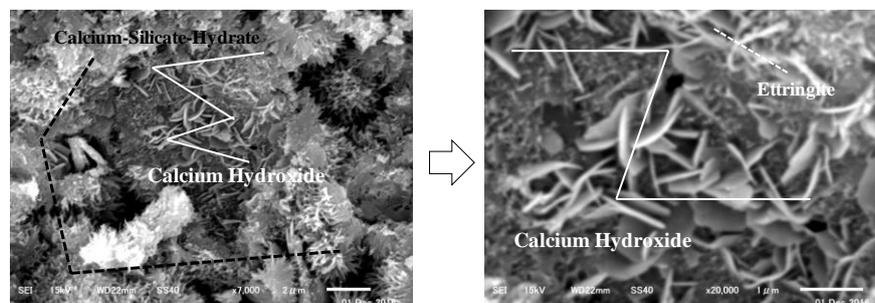


Figure 11. Hydration products under non-cracked area.

4. Conclusion

By focusing on the main self-healing precipitates of CaCO_3 crystals, we adjusted the temperature and pH and supplied carbon dioxide as nanometer-sized superfine bubbles into fine cracks to realize more precise self-healing. Moreover, by controlling crystal polymorphism to convert a cement solution of calcite into vaterite, various types of self-healing were evaluated. The findings in this research are shown below:

- (1) Under a self-healing condition in which a saturated $\text{Ca}(\text{OH})_2$ solution with CO_2 micro—and nanobubbles were supplied to cracked areas, the provision of Ca^{2+} and CO_3^{2-} facilitated the CaCO_3 reaction. Furthermore, it was determined that even cement material alone could demonstrate more effective self-healing performance in comparatively large cracks of more than 0.1 mm.
- (2) Vaterite, which contributed to the densification of cement matrix from the effect of void filling, was generated by providing nanometer-sized super-fine bubbles (average particle diameter: 50 nm) that included carbonate ion in the saturated $\text{Ca}(\text{OH})_2$ solution and by adjusting the water temperature to about 40°C and the pH to about 9.0 as the self-healing condition.

REFERENCES

- [1] Japan Concrete Institute: Practical Guideline for Investigation, Repair and Strengthening of Cracked Concrete Structure, Japan Concrete Institute, 2013, Tokyo, Japan (In Japanese).
- [2] Neville, A.M.: Properties of Concrete, Person Education Limited, p.328, 1995
- [3] Edvardsen, C.: Water Permeability and Autogenous Healing of Cracks in Concrete, ACI Materials Journal, Vol. 96, No. 96-M56, pp. 448-454, 1999
- [4] Choi, H., Inoue, M., Kwon, S., Choi, H., and Lim, M.: Effective Crack Control of Concrete by Self-Healing of Cementitious Composites Using Synthetic Fiber, Journal of the Materials, Vol. 9 No. 4, pp.1-14, 2016.
- [5] Matsumoto, M.: Polymorph control of calcium carbonate by reactive crystallization using microbubble technique, Chemical Engineering Research and Design, Vol. 88, No.12, pp.1624-1630, 2010
- [6] Kojima, Y.: Controls of Polymorphism and Morphology of Calcium Carbonate Compounds Formed by Crystallizing Amorphous Calcium Carbonate Hydrate”, Journal of Ceramic Society of Japan, Vol. 102(12), 1994, pp. 1128-1136.
- [7] Taniguchi, S., Otani, J., Nishizaki, I.: A study on the new evaluation method for asphalt pavement materials using X-ray CT scanner, Jpn. Soc. Civil Eng. J. Pavement Eng, Vol. 15, 2010, pp. 41-48 (In Japanese).