CHLORIDE ION MEASUREMENT SYSTEM FOR RC STRUCTURE BY NEAR-INFRARED SPECTROSCOPY

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ABSTRACT: Aging deterioration of reinforced concrete structures is mainly due to chemical reactions of rebar corrosion, carbonation, alkali-aggregate reaction, and the like, whereas collection of chemical information is effective to accurately grasp these signs. The recently introduced nondestructive measurement method of chloride ion concentration using a near-infrared (NIR) spectroscopy system detects an NIR peak of Friedel’s salt that is immobilized on a concrete surface, followed by application of a multispectral method. Herein, a prototype of a small-scale, NIR spectroscopy system that does not require seismic isolation was developed, using imaging-type two-dimensional Fourier spectroscopy technology, and the applicability of two-dimensional imaging of chloride ion concentration on concrete surfaces by this system was evaluated. Apparently, measurement by the system could be performed in a short time and with measurable accuracy. Moreover, the two-dimensional imaging of chloride ion concentration was possible in an outdoor environment with almost no associated difficulty. In addition to measuring Friedel’s salt, it was possible to observe cracks on the concrete surface by measuring water.

Keywords: Two-dimensional imaging, Chloride ion concentration, Near-infrared spectroscopy, Nondestructive measurement

1. INTRODUCTION

Since its period of economic boost, Japan has been engaged in the fast-paced reconstruction of social infrastructures that are reportedly estimated at present to cost around 800 trillion yen. Measures to slow down the aging of buildings and structural units is of dire need. Implementation of deterioration measures presupposes the collection of information on signs of degradation before deterioration and preventive maintenance measures. Present-day nondestructive inspections, however, which carry out every five years, such as visual inspection and concrete hammering test, are geared to obtaining information after deterioration. Time-related deterioration is mainly due to chemical wear-and-tear, i.e., corrosion, where chemical information is of vivid necessity for understanding the signs and pinpoint the source.

Nondestructive measurement of chloride ion on a concrete surface via near-infrared (NIR) spectroscopy is a recently developed method of collecting chemical information relative to deterioration of structures, which emerged subsequently after the discovery of the NIR peak of Friedel’s salt immobilized on concrete surface by Dr. Kanada, followed by practical application of the multispectral method [1-3]. A new NIR spectroscopy system is introduced in this paper, mainly to perform the objectives of measuring chloride ion concentration and moisture content on a concrete surface, and then the applicability of two-dimensional imaging obtained from the spectrum data is reported [4-6].

2. NIR SPECTROSCOPY SYSTEM

2.1 Overview of the Conventional System

So far, with the spectroscopic measurement in the outer region of the NIR, the 1300–2350 nm band could not be covered with high sensitivity and two dimensions due to the characteristics of the detector. It was confirmed that the imaging-type two-dimensional Fourier spectroscopy technology developed by one of the authors, Prof. Ishimaru, could cover the required wavelength band cited [7,8].

In the conventional mechanism, if this instrument receives vibration during measurement, the mirror is shifted, and interference does not occur. The proposed method overcomes the disadvantage in that spectral data cannot be acquired and thus, is suitable for on-site measurements.

Additionally, an angle of view correction function to correct the error caused by the difference
in optical path length caused by the difference in the
pixel position of the camera, as illustrated in Fig. 1,
was implemented.
Consequently, the conventionally used
demonstration machine was reduced to 203.5 × 398
× 140.5 mm; its original mass of 9.0 kg with camera
was lessened to 7.1 kg, and from 6.5 to 2.5 kg in the
spectroscopy section alone, thus, showcasing
improved portability [9].

Fig. 1 Field angle correction technology of imaging-
type two-dimensional Fourier spectroscopic
technique

3. INDOOR MEASUREMENT

3.1 Outline of Indoor Measurement

Indoor measurements for mortar specimens was
carried out to validate the accuracy of the system.
Ordinary Portland cement (OPC) and blast furnace
cement B (BB) were the cement samples
considered. The water–cement ratio applied was 50
%, whereas the fine aggregate in the mortar
specimens had a volume ratio of 48 %. Sodium
chloride was added in specimens. The chloride ion
concentrations are 0, 1, 2, 3, 4, 5, 10, 15, 20, 30
kg/m³. Thirty plastic molds (10× 30 cm in size)
were used for 10 kinds of specimens (3 molds each).
Sealed curing was performed in a 20 °C
environment for 7 days, before the molded
specimens were exposed indoors. Specifically, the
specimens were named according to the
combination of cement type and chloride ion
concentration. For example, an OPC paste sample
with chloride concentration of 1 kg/m³ was labeled
as NP01, whereas a BB 30 kg/m³ of chloride ion
concentration is labeled as BBM30 [10].

3.2 Indoor Measurement

The indoor measurements followed a schematic
procedure depicted in Fig. 2. A standard reflector
with 99 % reflectance was the reference, and a spot
heater unit was used for illumination. A high-
resolution SWIR lens was attached to the objective
lens of the instrument, and measurement was
performed at a sample angle of 0 degree and an
illumination angle of 45 degrees to the sample.

Fig. 2 Setup for indoor measurement

3.3 Measurement Results

Spectrum data of the specimens with each
chloride ion concentration were examined. The
relationship between the chloride concentration of
the specimen and the absorbance value in the
absorption wavelength range derived from Friedel’s
salt is shown in Fig. 3. Note that the absorbance
value for 20 and 30 kg/m³ of chloride concentration
for the same specimen was almost identical,
probably because the chloride fixed to the cement
was saturated. Except for the 30 kg/m³, the one for
which the calibration curve was prepared is
represented as a dotted line in the figure. The
coefficient of determination was 0.9272.

It is considered that this calibration curve can
estimate the chloride amount with high accuracy
from the peak value of the absorbance of Friedel’s
salt.

Fig. 3 Chloride concentration vs. absorbance of
specimens

3.4 Use of Two-Dimensional Imaging Software

Along with the development of this NIR camera
system was the creation of a two-dimensional
imaging software. Accordingly, specimens BBP0,
BBP30, and BBM30 were placed in a metal mortar
and manually (hand) made into a powder, prior to measurement. Sample output by the software is shown in Fig. 4.

The image on the left of the output plot was the result of the two-dimensional imaging, and that on the right side was the spectrum at five target points of the center in the left image. At the two-dimensional imaging, where the salinity is higher the color is closer to red and where the lower salinity is closer to blue.

(a) Absorbance 3.0
-1.5

(b) Absorbance 3.0
-1.5

(c) Absorbance 3.0
-1.5

Fig.4 Output of two-dimensional imaging; (a) powdered BBP0, (b) powdered BBP30, (c) powdered BBM30

For example, in BBP0, the chloride concentration was almost 0, and the heat map was blue almost entirely. In contrast, almost the whole area in BBP30 was uniformly yellow-to-red, given the high chloride concentration. In the case of BBM30, in which the specimen was hand-pulverized (and thus powderization was insufficient), the presence of uneven colors was observed. Very high concentration appeared near the center, and low-density parts locally occurred in the heat map. Since pulverization of the aggregate was not enough. Accordingly, the difference in the properties of the specimens is apparent in the two-dimensional imaging. It was confirmed that such a difference could be measured indoors with no associated difficulty.

4. APPLICABILITY VERIFICATION BY OUTDOOR MEASUREMENT

4.1 Objects and Measurement Outline

The target structure was once used near the coastal area of Shikoku Chuo City, removed for salt damage, and transferred to the Shikoku Technical Office, Shikoku Regional Development Bureau, Ministry of Land, Infrastructure, Transport, and Tourism. Of the hollow girder bridges, one girder that was not relatively salt-damaged (Fig. 5, near side, girder 1) and another from which concrete cover was peeled off due to salt damage (Fig. 5, back-side, girder 2) were used in the measurement. Prior to removal, the girders were 15.6 m long and had served for 51 years since they were built in 1967. The measurement was performed in summer.

The material of this girder is concrete. Therefore, the material is different from that of the calibration curve used in this part. However, it was assumed that the surface of the component was mostly cement paste or mortar, which was not substantially different from the material used to create the calibration curve.

Girder 2
Girder 1

Fig.5 PC digit removed due to salt damage

4.2 Measurement Results

Measurement values for girders 1 and 2 are provided in Fig. 6, respectively. Here, the heat map for girder 1 confirmed the appearance of yellow-to-red areas that were larger than those for girder 2, whereas the degree of salt damage and the tendency of the amount of surface chloride tended to almost
coincide. Moreover, the average values of the absorbance at the target points were respectively 0.32 and 0.41 for girders 1 and 2; it is considered that the difference in the degree of salt damage can be interpreted from the degree of the evaluation value.

Results of the Fourier transform infrared spectrophotometer (FTIR) analysis for the concrete powder that was scraped off the surface of the girder, to confirm the validity of the outdoor test, are displayed in Fig. 7. Moreover, the powder was collected from two places in girder 2, namely, girder 2-1 and girder 2-2. Although a clear peak could be confirmed in the portion indicated by the arrow in girder 1, this was not derived from Friedel’s salt.

On the contrary, in girders 2-1 and 2-2, the peak derived from Friedel’s salt could be confirmed in the part shown by the arrows in Fig. 7, thus, indicating that the result of outdoor measurement with the system is generally appropriate. However, regardless of the presence of the absorbance peak of Friedel’s salt, other peaks could be confirmed on the shorter wavelength side than that of the peak wavelength, which interferes with the result of absorbance of Friedel’s salt. Thus, a study on peak separation was conducted, with the aim of improving the system’s evaluation accuracy.

4.3 Improvement of Evaluation Accuracy by Peak Separation

The Friedel’s-salt-derived absorbance spectrum of the indoor test shows the difference from the baseline created from absorbance values of 2180 and 2290 nm. Apparently, the wavelength at which the peak was taken differed depending on the measurement cases. Although this is under investigation, this waveform is not the peak derived from Friedel’s salt. Therefore, assuming a Gaussian function, the waveforms not derived and that derived from Friedel’s salt were decidedly separated.

For example, shown in Fig. 8, at a specimen with a total chloride ion concentration of 10 kg/m³, both peaks could be separated by two Gaussian distributions. The absorbance after peak separation is shown in Fig. 9, and what prepared the standard curve using the absorbance value after peak separation is shown in Fig. 10.

Here, the coefficient of determination was 0.9658, and accuracy was greatly improved. The same peak separation scheme was imposed on the BB type specimens, and the result of preparing a calibration curve is shown in Fig. 11. Although not listed for the convenience of the paper, the coefficient of determination was 0.5494 before peak separation but rose to 0.7474 by peak separation. Such value of determination coefficient was small compared with that using OPC. The reason is under investigation.

A notable point in this measurement was the short measurement time. More specifically, the time required to obtain a single case of two-dimensional imaging results was approximately 60 s, including the time required for measurement on the imaging, which is much shorter than in conventional methods.
However, points that should pay attention are shown. Suspects of the progress of carbonation on the girder are typical, especially being constructed in a considerably long time, and such girders were also set outdoors for a long time in this study. With the system, the chloride content could be estimated from the amount of Friedel’s salt on the surface of the concrete; nonetheless, if Friedel’s salt gets liberated via carbonation, then the total amount of chloride actually attached to the surface of concrete may be larger than those confirmed by FTIR or the proposed system. Interestingly, the preparation of a calibration curve that takes into account the effect of Friedel’s salt release due to carbonation is a future direction for the present study.

Accordingly, approximately 1 cm of the test piece of the NP group was cut dry with a concrete cutter, and the cut surface was subjected to the proposed measurement system. Results are shown in Fig. 12. Here, the heat generated at the time of the cutting may have caused alteration of the Friedel’s salt; nonetheless, there were visible color shifts in the heat map from blue and green to yellow as the set chloride concentration increased. Based on the cross-sectional view of this specimen, two-dimensional imaging was possible.
4.4 Measurement regarding Water Distribution

In the NIR spectroscopy, a spectrum analysis on the OH group is frequently performed, especially on the spectrum of water. In this study, given that the concrete has water content, moisture measurement and imaging of water intrusion at the crack site were examined.

Using the proposed system, specimens that had been artificially cracked in advance were measured. A stone material with thermal expansion coefficients different from concrete was placed at the center of the specimen, and the specimen was heated to a maximum of 80 °C and then cooled. Cracks were generated due to the difference in the thermal expansion coefficients between the materials. The observed crack width was 0.15 mm at the top half and 0.10 mm at the bottom. Moisture content on the specimen was 3.3 %, as indicated by a concrete moisture meter.

Imaging results of the dried specimen are given at the left side in Fig. 13. Here, water was not confirmed in the original image of the NIR camera. After that, a specimen supplied with water from the outside by atomizing and re-imaged after visual confirmation that it had been substantially dried, is shown at the right side in Fig. 13. Moisture in the specimen could not be confirmed visually, but by imaging, this became possible with the moisture remaining in the crack. Here, moisture content was 4.3 %.

More accurately, through the proposed system, the presence of even the slightest amount of water adhering to concrete surface may be sufficient to make a proper evaluation, and fine cracks that cannot be grasped by visual inspection were shown. This issue is another direction for future study.

5. CONCLUSIONS

The NIS system presented in this paper was fundamentally geared to the measurement of chloride concentration on concrete surfaces and the evaluation of applicability of two-dimensional imaging of the chloride concentration. These points can be generalized from the findings: (1) A compact, non-seismic-free two-dimensional imaging spectrometer was developed using Fourier spectroscopy technology; (2) Because the peak waveform considered to be Friedel’s salt is adhered to a waveform other than it, waveform peak separation was essential to extract that of Friedel’s salt. Doing so, the determination coefficient of the calibration curve increased greatly; (3) The two-dimensional imaging for the chloride concentration in the cross section of the specimen could be performed in a short time and with high accuracy; (4) Moreover, the two-dimensional imaging of chloride concentration is possible for measurement in open air with no associated difficulty.
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