Non-destructive Inspection Methods for Componential Analysis of Concrete

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ABSTRACT

Many non-destructive inspection methods have recently been developed for concrete structures. However, these methods can obtain only physical information of concrete, such as crack depth, delamination or position of reinforcement etc. near its surface. If chemical information is required, sampling and componential analyses may be carried out. Non-destructive method that can detect deterioration factors such as carbonation, chloride content or sulfate attack would be an outstanding innovation in inspection methodologies. In this research, near-infrared spectroscopy and X-ray fluorescence analysis were applied for componential analysis for concrete. These methods are very effective compared to traditional methods, therefore, working efficiency and maintenance cost will be improved.

1. Introduction

Several componential analyses are used for concrete, for example, carbonated area can be colored by spraying phenolphthalein alcohol solution, potentiometric titration method is commonly used to measure the chloride content in concrete. EPMA (Electron Probe X-ray Microanalysis) may be applied for elemental analysis if detailed information is required. But the potentiometric titration method or EPMA require high labor and cost because pretreatment of sample and titration are troublesome tasks, and measurement results can not be obtained quickly. If deterioration factors could be measured by non-destructive inspection methods, this would be an effective technique for inspectors.

The authors are developing new non-destructive methods which can detect deterioration factors of concrete such as carbonation, chloride content or sulfate attack using near-infrared spectroscopic technique and portable X-ray fluorescence analyzer. This paper introduces the applicability of near-infrared spectroscopy and X-ray fluorescence analysis to detect deleterious substances of concrete.

2. Introduction of Near-infrared Spectroscopy

Near-infrared [NIR] spectroscopy had been developed in the area of agriculture or food. Electromagnetic waves are absorbed or reflected from any substance depending on the characteristics of their components, therefore, unknown components and their concentration can be estimated instantly if their optical properties are known. NIR spectroscopy has some advantages compared to traditional componential analyses. This method can measure objects directly and non-destructively without pretreatment of sample or chemical agent. This is an efficient, low-energy, pollution-free, environment-friendly, cost-effective inspection method.

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2.1 NIR Spectrum Change due to Deterioration of Concrete

Fig.1 shows spectrum changes due to deterioration of concrete. Increase of absorbance at 2266nm can be observed as chloride content increases. This behavior is attributed to the fact that the vibration mode of cement hydrates is changed by the action of chloride. 2266 nm can be selected as characteristic wavelength to quantify chloride content of cement paste.

Decrease of absorbance at 1410nm can be observed due to carbonation. $Ca(OH)_2$ in hydrated cement changes to $CaCO_3$, therefore, absorption properties of hydroxyl (-OH) were found absent. Absorption peak at the wavelength is caused by 1st overtone spectroscopy of the hydroxyl stretch vibration in calcium hydroxide. Wavelength of 1410nm can be selected as characteristic wavelength to verify carbonation.

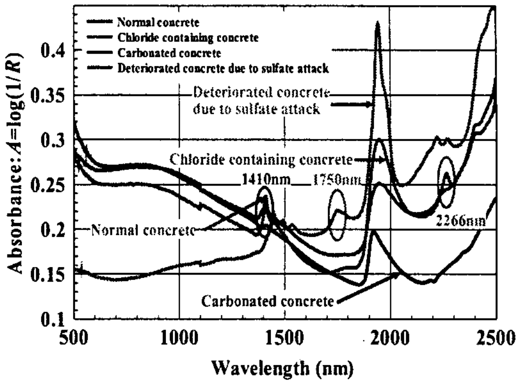

Fig. 1 NR Spectrum change due to deterioration of concrete

Deterioration due to sulfuric acid is often concern for sewage treatment equipments or structures in hot-spring area. Calcium sulfate dihydrate is produced due to chemical reactions between calcium hydroxide and sulfuric acid (equation 1).

$$Ca(OH)_2+H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O \qquad (1)$$

Some optical absorption peaks can be observed after deterioration due to sulfate attack and absorption peak at 1410nm was found to be absent due to neutralization. Wavelength 1750nm was selected as characteristic waveband to verify deterioration caused by sulfuric acid since compared to other peaks, it was independent and clear. These deterioration factors can be detected to verify the NIR spectrums at specific wavelengths and their concentrations can be estimated from the absorption properties.

2.2 Introduction of NIR Spectral Imaging System

NIR spectral imaging system was introduced in order to detect distribution or concentration of deterioration factors remotely. Deteriorated area can be detected to capture spectral image of specific wavelength because deleterious substance absorbs (reflects) NIR ray at the wavelength, then the area appears dark (bright). In case of chloride penetration, chloride containing cement paste absorbs NIR ray of 2266nm, so high chloride concentration area is captured as dark. Similarly, carbonated area appears bright when spectral image of 1410nm is captured, and sulfate attacked area appears dark by capturing spectral image at 1750nm.

Fig.2 shows actual scanning of NIR spectral image of mortar specimen which has high chloride content area of shape:A. Left picture was captured by normal digital still camera (visible range), right picture was captured by NIR spectral imaging system. Distribution of chloride content can be seen by analyzing captured spectral image.

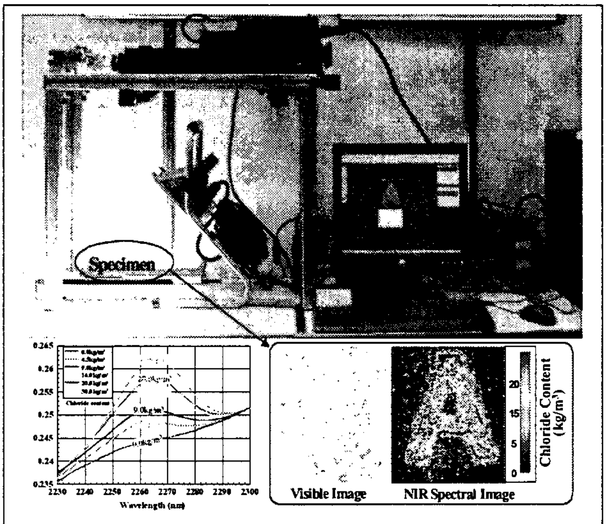

Fig. 2 Visualization of high chloride content area by NIR spectral imaging system

3. Introduction of X-ray Fluorescence Analysis

X-ray fluorescence [XRF] analysis is a non-destructive analytical technique used to determine the elemental composition of a sample. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing non-destructive measurement of the elemental composition of a sample.

3.1 Principle of XRF Analysis

When a primary X-ray excitation beam from an X-ray tube or a radioactive source strikes a sample, the X-ray can either be absorbed by the atom or scattered through the material. During this process, if the primary X-ray has sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic X-ray whose energy is the difference between the two binding energies of the corresponding shells. The process of emissions of characteristic X-rays is called as X-ray fluorescence. Qualitative analysis can be carried out from spectrum of energy and their concentration can be obtained from the intensity of X-ray fluorescence from sample.

3.2 Detection of Deleterious Substances of Concrete by XRF Analysis

Steel corrosion due to chloride penetration is often a concern for reinforced concrete structures exposed to seashore environments, and sulfur is recognized as harmful substance for concrete structures. Chlorine can be detected from the XRF spectrum at 2.621keV. As shown in Fig.3, the number of XRF counts at 2.621keV increases as chloride content increases. The calibration curve should be prepared to carry out quantitative analysis. Fig.4 shows high correlation between chloride content and peak area corresponding to chlorine. Chloride content of a sample can be estimated by substituting its peak area into the calibration curve (Fig.4). In XRF analysis, in principle, total chloride content of concrete (free and fixed chloride) can be measured.

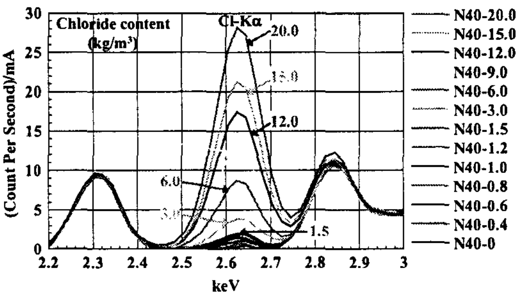

Fig. 3 Relationship between chloride content and XRF counts

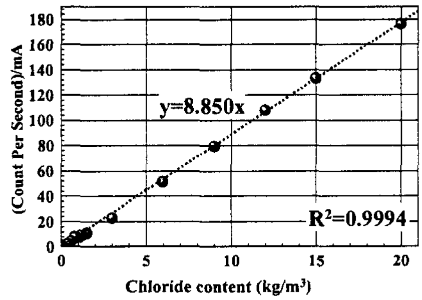

Fig 4. Relationship between chloride content and peak area corresponding to chlorine

Sulfur can be detected from the XRF spectrum at 2.307keV. Fig.5 shows the spectrum change after deterioration due to sulfuric acid attack. The number of XRF counts at 2.307keV corresponding to sulfur increases after deterioration, and as the counts of calcium decreases, the counts of silicon increases due to exposure of aggregates because cement paste is dissolved.

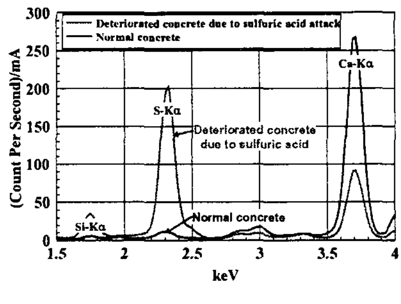

Fig. 5 Spectrum change due to sulfuric acid attack

4. Application of Actual Measurement

The advantage of these methods is their application to on-site

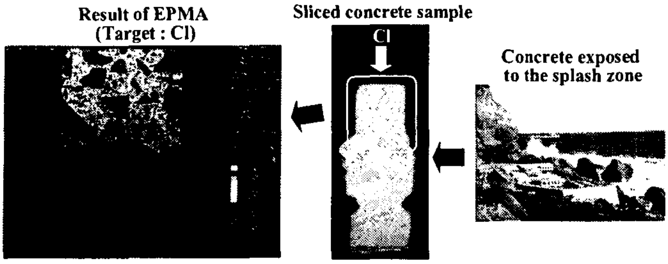

Fig. 6 Result of EPMA of concrete specimen exposed to the splash zone

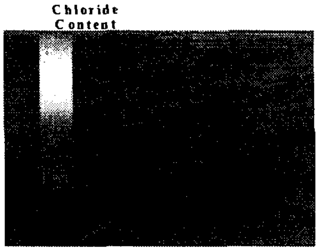

Fig. 7 Chloride distribution captured by NIR spectral imaging system

measurement. EPMA is commonly applied, however, processes of polishing or metal evaporation coating are required before analysis, so results can not be obtained quickly. NIR spectral imaging system may be used as alternative procedure of EPMA, and may be able to reduce the analysis time.

Fig.7 shows the chloride distribution of a sliced concrete specimen exposed to the splash zone. It was observed that chloride penetrated from the top surface. Good agreement of penetration area detected by spectral image and result of EPMA (Fig.6) was observed.

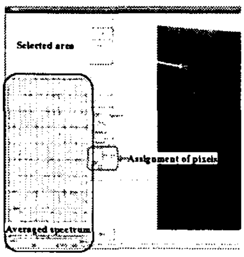

Fig. 8 Control system of NIR spectral imaging system

Fig. 9 Measurement of cutting plane by portable XRF analyzer

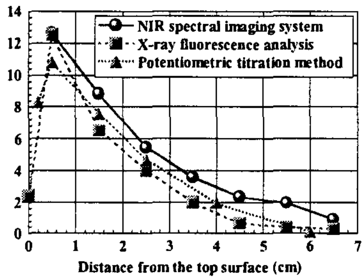

Fig.10 Distribution of chloride content

The analysis software of NIR spectral imaging system delivers a function to output average spectrum of selected area (Fig.8). Therefore chloride content of an arbitrary portion can be measured to analyze averaged spectrum on the software. As shown in Fig.9, analysis of the concrete plane, using portable XRF analyzer, can be carried out by contact of the sample stage with the plane. The average of three measurement points (other than coarse aggregate) at each depth were plotted in Fig.10. Values obtained by potentiometric titration method were also plotted for reference. The same trend can be observed between these methods and traditional method. Therefore, applicability has been corroborated by experimental results.

5. Conclusions

Applicability of NIR spectroscopy and portable XRF analyzer to componential analysis was confirmed from the experimental results. It has been shown that distribution of deleterious substances can be detected from the spectral images and the content can be measured using portable XRF analyzer. These methods can be chosen as the situation demands, and shorten measurement time and improve working efficiency. These will prove to be powerful tools for inspectors or administrators of infrastructures.