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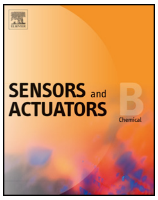

Research Paper

A Raman spectroscopy based optical fibre system for detecting carbonation profile of cementitious materials

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ABSTRACT

Sensors demonstrate huge potential in civil engineering for monitoring the health condition and performance of concrete structures. Amongst various chemical deterioration mechanisms causing inadequate durability of concrete structures, carbonation is one of the most severe mechanisms. It occurs from the chemical reactions between intruded CO_2 and calcium-bearing phases, hence is accompanied by the formation of calcium carbonate ($CaCO_3$) and the decrease of the alkalinity of concrete pore solution, causing corrosion of rebar in concrete. Thus, detecting carbonation process, especially, determining the carbonation profile (i.e. the content of carbonation products formed against the depth into concrete structure), is of great importance to the diagnosis of the health condition of concrete structures and the prediction of service life. Unfortunately, existing sensors for health monitoring systems suffer from various limitations. Optical fibre Raman technology offers a unique opportunity for developing a novel chemical sensor system capable of monitoring the service-condition of concrete in situ. In the current work, a bespoke ‘coaxial’ optical fibre sensing platform based on Raman spectroscopy was successfully established with a 514.5 nm laser. All the optics were tailored for efficiently exciting and receiving signals from cementitious materials, and their diameters were restricted within 0.5 in. in order to explore the feasibility of developing an embeddable miniature sensor system in the future. This sensing system was then employed to detect the carbonation mechanism of a plain Portland cement (PC) paste. The calcium carbonate polymorphs as well as the carbonation profile in the PC paste was successfully recognised and established with the results being verified favourably by bench-mounted Raman, X-ray Diffraction (XRD) and Thermogravimetry (TG) analyses. Our results demonstrate a good potential for developing a novel Raman spectroscopy based optical fibre sensor system for monitoring the health condition and the performance of concrete structures in future.

1. Introduction

Recent decades have witnessed some interest in developing sensor devices for monitoring the physical properties (e.g., strain) of concrete structures [1,2]. However, as concrete are exposed to different environment (such as CO_2 and SO_4^{2-}), it would trigger chemical deteriorations due to the interaction between concrete and exposure environment. Monitoring the changes of internal chemistry of concrete is, hence, more important as this can provide insight into the cause and evolution of the deterioration mechanisms as well as the prediction of health-condition and performance of concrete structures [3]. Amongst the various deterioration mechanisms initiating the durability issues of concrete structures, carbonation is a severe deterioration mechanism causing the inadequate durability of reinforced concrete [3,4]. It is mainly a chemical process occurred when the calcium-bearing phases, such as calcium hydroxide (CH), calcium silicate hydrate (CSH) and various calcium aluminate or ferro-aluminate hydrates, in cement matrix are attacked by carbon dioxide (CO_2) penetrated into concrete through the pore network [5–8]. The dominant reaction is the one between calcium hydroxide [$Ca(OH)_2$] and CO_3^{2-} (i.e., the carbon dioxide dissolved in concrete pore solution) to form calcium carbonate ($CaCO_3$). This process lowers the pH of concrete pore solution from about 13–8.3, in the case of complete carbonation [9,10]. At this pH level, the passive film formed on the surface of steel bar could be destroyed, leading to the ini-

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tiation of the corrosion of rebar in the presence of oxygen and moisture [3,10]. Additionally, CSH gel could also be attacked, leading to a reduction of Ca/Si ratio from around 1.75 to a lower value of 0.67 at the early stage of carbonation, followed by a subsequent transformation into calcium carbonate and amorphous silica gel by further carbonation [5,11]. Although this reaction, unlike the carbonation of calcium hydroxide, does not affect the alkalinity of pore solution, it favours the decomposition of CSH and, hence, reduces the stability and strength-carrying capacity of cement matrix. Obviously, carbonation changes the cement chemistry of the internal concrete remarkably, with the most prominent aspect of forming calcium carbonate [12]. The calcium carbonate phases precipitated within the cementitious materials could exist in different polymorphs, such as, calcite (well-crystallised phase) and vaterite/aragonite (poor-crystallised phases) [12,13]. Generally, the content of calcium carbonate decreases with increasing distance from the exposed surface of concrete, which is caused by the decreased degree of carbonation due to the reduced penetration of CO_2 into the interior part of concrete [14–16]. However, with increased exposure to CO_2-bearing environment, the depth of carbonation increases with time. As it is the cover concrete which provides the protection to the embedded rebar, differentiating the type of calcium carbonate polymorphs formed within the cover concrete, but more importantly, determining the carbonation profile in terms of the content of calcium carbonate phases over the depth of cover concrete and also over time, is of great importance for predicting the service life of concrete structures [17]. Moreover, it can provide valuable information for the diagnosis of health condition of concrete structures so that timely actions could be taken before any severe damages could be initiated.

Numerous studies have been reported in the literature on the investigation of concrete carbonation [12,13,15,18–21]. The phenolphthalein spray test, by spraying phenolphthalein indicator solution onto a freshly exposed concrete surface and visually inspect the sprayed section, is probably the most well-known method to assess the carbonation depth of concrete [19,22]. As phenolphthalein turns purple at about $pH > 8.3$ and remains colourless when $pH \leq 8.3$, the deep-purple colour on the uncarbonated area and the clear area of the carbonated region on the surface of concrete can be immediately differentiated [23,24]. This test is convenient, quick and cheap. However, although this test can give reproducible results to indicate the fully carbonated region, it cannot differentiate the boundary between uncarbonated and partially carbonated concrete or the boundary between partially carbonated and fully carbonated concrete where pH may have only dropped to around 10–12 [25]. It is, therefore, generally accepted that the phenolphthalein method may underestimate the carbonation front [26,27]. To address this issue, researchers have attempted to employ other techniques to study the carbonation in cementitious materials, including Thermogravimetry (TG)/Derivative Thermogravimetry (DTG) [12,15,20], X-ray Diffraction (XRD) [12,13], Fourier transform infrared spectroscopy (FTIR) [18,19,26], Gammadensimetry [15,21] and Mercury Intrusion Porosimetry (MIP) [28,29]. However, most of these methods are laboratory based and sample need to be taken from the structures, even though it only causes little damage to the structure. To obtain non-destructive, continuous and real-time information about the condition of concrete structure, there is an increasing interest and rapid advancement in developing sensor system for monitoring the chemical environment of concrete, such as carbonation/pH profile, especially within the cover zone [30–32]. Amongst the sensors capable of monitoring the properties of cover concrete, electrical sensors (ES) have attracted tremendous attentions and the most widely used is electrical resistance based sensor, such as covercrete electrode array (CEA) [32,33]. CEA measures the conductance, or resistance, across the electrode pairs mounted at discrete depths in cover-zone and, hence, give valuable insight into the spatially distributed moisture and ionic movement within the cover concrete. However, the limitation associated with the ES mainly lies in its inadequacy in differentiating, uniquely, each individual deterioration mechanism, such as carbonation, as the electrical properties of concrete can also be affected by other factors such as moisture change, ions ingress and ongoing hydration. Due to this reason, fibre optic sensors (FOS) have attracted tremendous attentions in recent years for its merits of inert nature, immunity to electromagnetic interference, lightweight/miniature and multiplexing into multi-sensing [34–36]. More importantly, FOS can overcome the drawback of ES by encapsulating the fibre tip with specific chemical dyes so that each individual deterioration mechanism can be uniquely differentiated [30,36–38]. For example, fibre optic pH sensor has demonstrated its potential in following the pH variation in concrete due to carbonation and this could provide some timely information on the progress of carbonation within the cover concrete [30,37]. However, FOS suffers from its irreversibility and instability of the chemical dyes in the inherently aggressive environment of the pore solution of concrete [36,39]. On the other hand, attempts have also been made by the researchers to monitor the condition of rebars in concrete directly, such as the Anode-Ladder system developed by P. Schießl and M. Raupach, which can be used to monitor the galvanic current between the pairs of anode-cathode and hence, can provide invaluable information on the corrosion rate of the rebars [40,41]. Although this system also can provide an early warning of the possible corrosion, it cannot provide the information needed to understand the chemical reactions incurred in cover concrete. Hence, there is still a need to develop a more reliable and robust sensor system which can be used to effectively monitor the health condition and the performance, in particular the possible chemical reaction involved, of concrete structures subjected to different deterioration mechanisms, such as carbonation.

Since 1970's, Raman spectroscopy has attracted increasing attentions worldwide in analysing various phases in cement and concrete area due to its fingerprint characterisation capacity based on the measurement of the vibrational spectra of analytes [42–49]. In particular, Raman spectroscopy has demonstrated its unique capability to identify different calcium carbonate polymorphs, such as calcite, vaterite and aragonite [50–58]. In recent years, by combining the qualitative/quantitative characterisation capability of Raman spectroscopy and the light transmission of optical fibres, optical fibre Raman technology has shown its potential as a next-generation sensing system. Above all, the rapid developments of instrumentation, such as the portable Raman spectrometer, the long-distance and low-loss optical fibre and some sophisticated functional optics, offer a huge potential for a monitoring system based on optical fibre Raman spectroscopy technology and, indeed, researchers have already been exploring its applications in the areas such as biomedical diagnosis [59,60], chemistry process monitoring [61,62] and operations in detrimental environment [63,64]. However, surprisingly, this technique is not currently being attempted in the area of cement and concrete. During the past few years, the authors have been taking the initiative to explore the potential of developing an optical fibre Raman sensing system to characterise the deterioration mechanisms of cementitious materials, with an ultimate target to develop a Raman spectroscopy based embeddable optical fibre sensor network capable of monitoring and evaluating the health condition and the performance of concrete structures on site. Our preliminary work have confirmed the feasibility of characterising the deterioration products formed during the sulphate and carbonation attacks in hardened cement paste by a tailored fibre-optic excitation pathway (e.g., fibre excitation path + objective collection) [65,66]. However, to fully verify the feasibility of developing a future fibre optic Raman based sen-