Cement and Concrete Research 42 (2012) 95–98

Contents lists available at SciVerse ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

# In situ measurement of the transport processes of corrosive species through a mortar layer by FTIR-MIR

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ARTICLE INFO

*Article history:*
Received 29 May 2010
Accepted 17 August 2011

*Keywords:*
FTIR-MIR
Mortar (E)
Transport Properties(C)
Degradation(C)

ABSTRACT

Fourier Transform Infrared Spectroscopy with Multiple Internal Reflection mode (FTIR-MIR) has been applied for the first time to in situ follow the transport process of corrosive species through a mortar layer and their accumulation at the internal reflection element (IRE)/mortar interface. The kinetic processes of $H_2O$ and $SO_4^{2-}$ transport through the mortar specimens with different curing time were studied. The results indicated that $H_2O$ and $SO_4^{2-}$ presented different transport behavior through the mortar layer. Adding $Na_2SO_4$ into distilled water resulted in a slower transport rate of $H_2O$. And the curing time of mortar had a significant effect on its permeability. The in situ FTIR-MIR measurement was proved to be able to provide reliable information on the interface and the transport process through mortar.

## 1. Introduction

Premature degradation of reinforced concrete structures has become a serious problem in modern society [1,2]. It is believed that degradation of reinforced concrete is initiated by the penetration of aggressive species such as water, chloride ions, oxygen, carbon dioxide and sulfate [3,4]. The accumulation of these aggressive species in the concrete and at the steel/concrete interface would cause severe effects, and finally lead to the degradation of reinforced concrete system. For example, sulfate ingress will result in disruptive expansion of the cement matrix, and significant loss of mechanical strength [5–7]. There is also evidence to show that sulfate ions have a destructive effect on the steel bar directly [8,9]. Thus, the measurement of the transport behavior of corrosive species and the permeability of concrete is important for damage prediction and assessment previous to repair works, and for quality control of reinforced concrete structures.

Many techniques have been developed for studying the transport behavior of corrosive species and evaluating the permeability of concrete or mortar, such as flow/weight measurement, chemical analysis, electrical charge amount method and probes [10–13]. Though some of these methods are widely used till now, they suffer some drawbacks. For example, flow/weight measurement is not sensitive enough; chemical analysis is always destructive, inconvenient, and cannot provide instantaneous information, electrical charge amount method can only measure the amount of all the ions instead of a specific ion; and the probes are not stable and durable enough in concrete [13–16]. Thus, attempts to develop the facile in-situ monitoring methods with high sensitivity are needed to further understand the transport behavior of corrosive species through concrete layer and their effects on the degradation of reinforced concrete structure.

The key strategy of this work is using the Fourier Transform Infrared Spectroscopy with Multiple Internal Reflection mode (FTIR-MIR), which is able to offer a number of advantages for detecting aggressive species: (1) it is of spectroscopic sensitivity to water, sulfate ion, and groups or bindings of most inhibitors; (2) it is able to detect all the IR sensitive species simultaneously and distinguish them as long as their peaks are not overlapped; (3) it can be used at ambient condition, and thus, is suitable for in situ and nondestructive measurement.

This paper demonstrates that the in situ FTIR-MIR method is a novel and powerful technique in studying the accumulation of corrosive species (such as $H_2O$ and $SO_4^{2-}$) at IRE/mortar interface and their transport behavior through a mortar layer, which is critical for further understanding the premature degradation of reinforced concrete structure in service environments.

## 2. Experimental

### 2.1. Preparation of mortar specimens

The mortar specimens were prepared by mixing ordinary Portland cement, distilled water and fine sand with a maximum size of 1.5 mm. The sand/cement ratio was 1.5, and the water/cement ratio was 0.3. The mortar was filled and tamped in the mold carefully to get the specimen in the required thickness of 2.5 mm. After 24 h of the pre-curing, mortar specimens were demoulded and further

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doi:10.1016/j.cemconres.2011.08.007

cured in a 100% relative humidity environment for 7, 14, and 28 days. After completely curing, the mortar specimens were cut into 50 × 10 × 2.5 mm and to be dried at air-conditioned room temperature (25 °C) and humidity (45%) for 2 days.

### 2.2. In situ measurement of $H_2O$ and $SO_4^{2-}$ at IRE/mortar interface

The measurements of $H_2O$ and $SO_4^{2-}$ at IRE/mortar interface were carried out using Thermo Nicolet 380 FTIR spectrometer with an ATR (attenuated total reflection) accessory. Fig. 1 shows the specimen configuration and experimental setup. The internal reflection element (IRE) was 60 × 10 × 2.5 mm spectroscopic grade, 45° parallelogram germanium (Ge) piece. A mortar specimen with an electrolyte chamber attached was applied to the surface of the IRE and placed vertically in the ATR accessory holder. FTIR-MIR spectra in the 4000–900 $cm^{-1}$ region were collected before electrolyte was added. The same measurements were subsequently done after exposure to electrolyte at different time intervals without disturbing the optical alignment of the instrument. The Scan times are 16 and the resolution is 8 $cm^{-1}$. Each spectrum was obtained by subtracting the spectrum from the corresponding background spectrum. All experiments were carried out under the static conditions at air-conditioned room temperature (25 °C) and humidity (45%).

## 3. Results and discussion

### 3.1. Transport behavior of $Na_2SO_4$ solution through a mortar layer

Fig. 2 presents FTIR-MIR spectra at IRE/mortar interface during the exposure of the mortar layer to 0.5 mol/L $Na_2SO_4$ solution for different time intervals. The mortar specimens used were cured for 7 days. The bands peaking near 3400 and 1640 $cm^{-1}$ in the spectra are responded to OH stretching and bending modes, respectively. The band peaking near 1150 $cm^{-1}$ is due to $SO_4^{2-}$ stretching mode [17]. The intensity of the OH and $SO_4^{2-}$ bands increased with time of exposure to $Na_2SO_4$ solution. These changes were attributed to the penetration of $H_2O$ and $SO_4^{2-}$ from the solution through the mortar layer to IRE/mortar interfacial region.

Fig. 3 shows the intensity changes of the 3400 and 1150 $cm^{-1}$ bands as functions of exposure time. The intensity, expressed as peak area, is proportional to the amount of detected $H_2O$ and $SO_4^{2-}$ respectively. The 3400 $cm^{-1}$ band was chosen for the water quantitative analysis, because the OH bending mode at 1640 $cm^{-1}$ is not sensitive enough to low water concentration [18]. Two important features can be observed by the comparison of Fig. 3a and b. First, in the initial period, (depicted by the two smaller dotted symbols) the intensity of water increased more quickly than that of $SO_4^{2-}$. There are three possible explanations to this observation: (a) compared to water, $SO_4^{2-}$ ions are difficult to transport due to their big volumes; (b) $SO_4^{2-}$ ions react with hydrated cement paste and thus the amount of free ions decrease; (c) $SO_4^{2-}$ has lower IR sensitivity than water [19].

Second, after exposure to $Na_2SO_4$ solution for about 40 h, the increase of water intensity was unobservable while the intensity of $SO_4^{2-}$ was still increasing. This phenomenon can be explained by the different transport mechanisms of $H_2O$ and $SO_4^{2-}$: the movement of water through unsaturated mortar is mainly caused by capillary suction. And

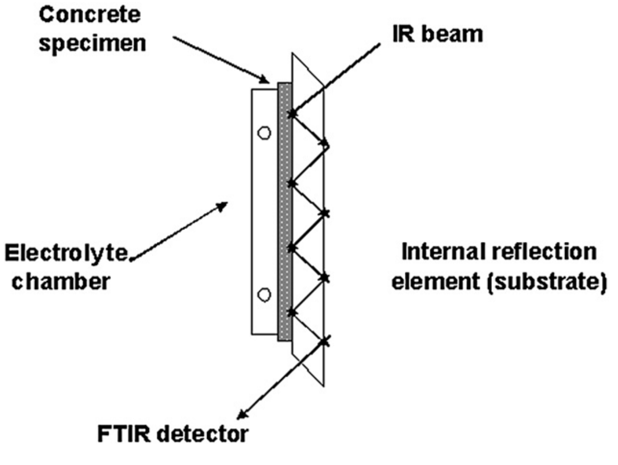

**Fig. 1.** Experimental set up for in situ measurement of $H_2O$ and $SO_4^{2-}$ at substrate/concrete interface.

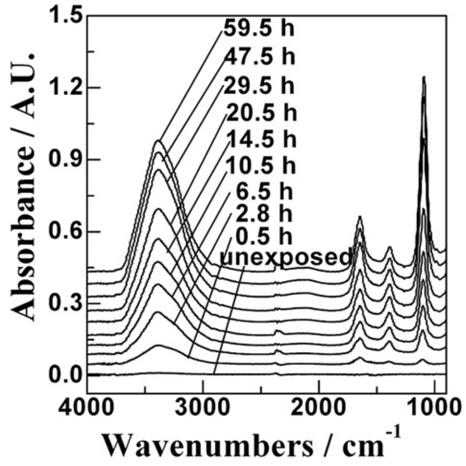

**Fig. 2.** FTIR-MIR spectra during exposure to 0.5 mol/L $Na_2SO_4$ solution for concrete specimens cured for 7 days.

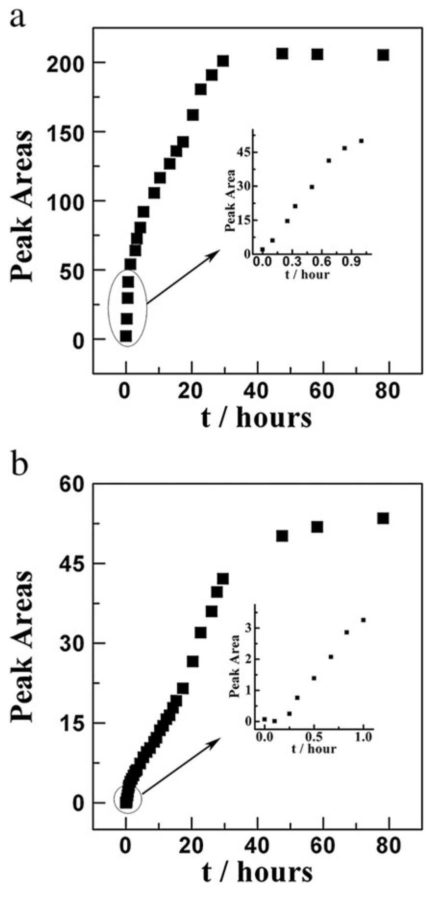

**Fig. 3.** Intensity changes of $OH^-$ and $SO_4^{2-}$ bands as functions of exposure time: (a) $OH^-$; (b) $SO_4^{2-}$. ■ the whole sequence; ● the initial period.

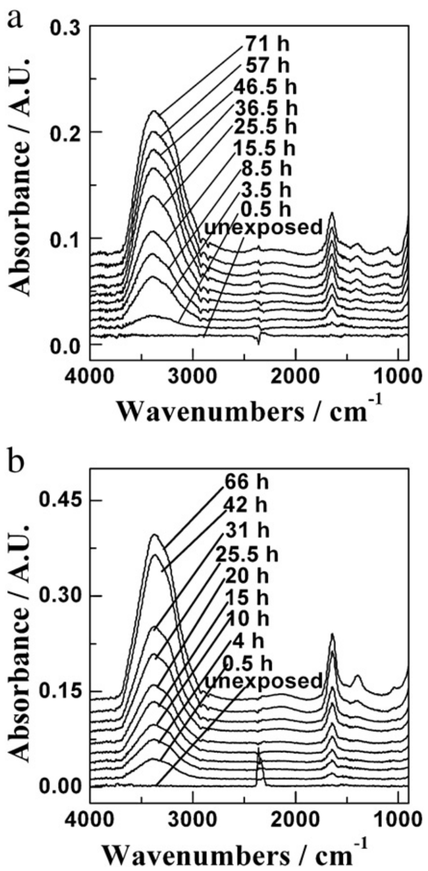

**Fig. 4.** FTIR-MIR spectra during exposure of concrete specimens cured for 28 days to (a) 0.5 mol/L $Na_2SO_4$ solution and (b) distilled water.

the transportation of sulfate ions through unsaturated mortar involves both diffusion and advection caused by a capillary suction flow [20,21]. After the transport of water reached its equilibrium state, sulfate ions stopped transporting by advection, but the diffusion was still occurring. This was because sulfate ions moved slower than water, which resulted in concentration gradient through the mortar layer.

### *3.2. Different transport behavior between distilled water and $H_2O$ in sodium sulfate solution*

Fig. 4 shows FTIR-MIR spectra of distilled water and $H_2O$ in 0.5 mol/L $Na_2SO_4$ solution transport through the mortar layers of 2.5 mm thickness for different time intervals. The mortar specimens used here were cured for 28 days. Fig. 5 shows the intensity changes of the OH stretching band in distilled water and sodium sulfate solution, as functions of exposure time. It is interesting to note that the transport behavior and transport rates of $H_2O$ in distilled water and in sodium sulfate solution through the mortar specimens were almost the same in the initial period. But after a span of time, the transport rate for $H_2O$ in $Na_2SO_4$ solution was obviously slower than that for distilled water. This differentiation was attributed to the influence of $Na_2SO_4$ in the solution [22]. It can be explained by: (a) the adding of $Na_2SO_4$ increased the viscosity of the solution and resulted in a

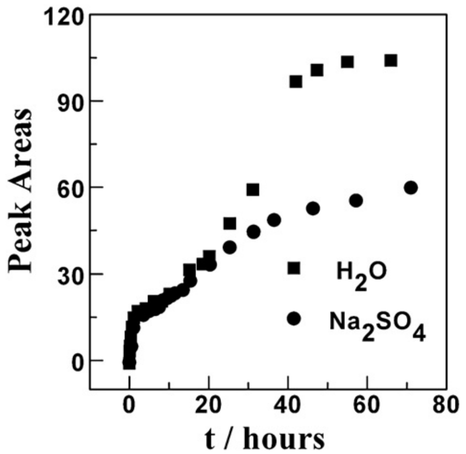

**Fig. 5.** Intensity changes of the water band in the case of distilled water and sodium sulfate solution, as functions of exposure time.

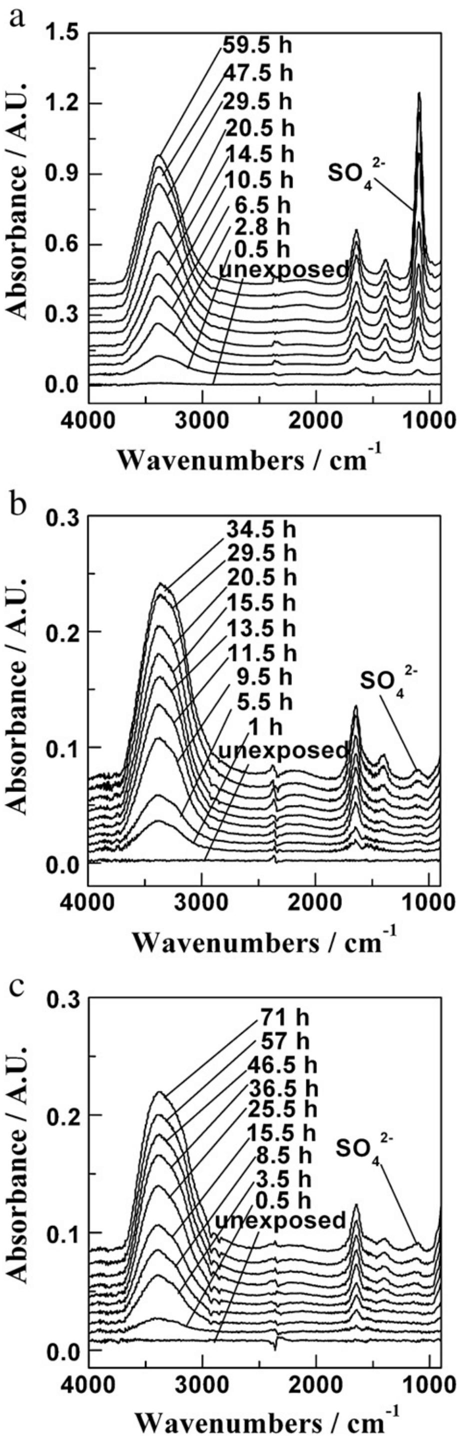

**Fig. 6.** FTIR-MIR spectra during exposure to 0.5 mol/L $Na_2SO_4$ solution for concrete specimens with different curing times: (a) 7 days; (b) 14 days; (c) 28 days.

slower transport rate [23]; (b) $SO_4^{2-}$ reacted with the cement hydration products, formed gypsum or ettringite at some location and decreased local porosity, thus reducing the effective paths, where corrosive chemicals were able to transport [24–26].

### *3.3. Effect of curing time on the permeability of mortar specimens exposed to $Na_2SO_4$ solution*

Fig. 6 shows FTIR-MIR spectra for 0.5 mol/L $Na_2SO_4$ solution transport through mortar specimens with different curing time at various exposure intervals. It can be observed from the spectra that the amount of $H_2O$ and $SO_4^{2-}$ accumulated at the IRE/mortar interface decreased with the extension of curing time. And the difference between mortar specimens cured for 7 days and 14 days was greater than that between mortar specimens cured for 14 days and 28 days. Those results reveal that the permeability of mortar specimens tends to be lower with the extension of curing time. Because during the curing process, hydration products of cement fill and obstruct the internal micro pores and capillaries of mortar, and thus lower the permeability of mortar [27]. However, the hydration rate decreases with time, so there exists an optimum curing time considering both the permeability of mortar specimens and the saving of time and energy.

## 4. Conclusions

(1) The Fourier Transform Infrared Spectroscopy with Multiple Internal Reflection mode (FTIR-MIR) was demonstrated to be a sensitive and powerful tool for in situ measurement of the transportation and accumulation of aggressive species through the mortar layer.

(2) $H_2O$ and $SO_4^{2-}$ possessed different transport behavior through the mortar layer. The movement of $H_2O$ through unsaturated mortar was mainly caused by capillary suction. The movement of $SO_4^{2-}$ through unsaturated mortar should take into account diffusion, advection caused by a capillary suction flow and the reaction between $SO_4^{2-}$ and the cement hydration products. The adding of $Na_2SO_4$ in distilled water resulted in a slower transport rate of $H_2O$.

(3) The curing time had a significant effect on the permeability of mortar specimens. The longer the curing time, the lower the permeability of the mortar. However, there existed an optimum curing time considering both the permeability of mortar specimens and the saving of time and energy.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50731004, 21021002) and the National High Key Technology R&D Program of China (Grant No. 2007BAB27B04).

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