Fluorescence-Based Fiber Optic Sulphate Sensor for Long Term Sulphate Ion Monitoring in Concrete Structures

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ABSTRACT

Concrete has been one of the most popular construction materials around the world. However, sulphate ion will cause of concrete degradation and lead to the decrease of service life of concrete structures. The formation of ettringite and other reaction products can lead to the decrease of service life of concrete structures, thus, a continuous monitoring of sulphate ions is needed as a reference for the maintenance work of concrete structures. This paper presents the design and development of a fluorescence-based fiber optic sulphate sensor for this purpose. The sensor's design capitalizes on the changes in fluorescent intensity of morin-metal ion complexes induced by sulphate concentration changes. By using cellulose acetate, the complex is transformed from a solution to a thin film, serving as the sensing element in the sensor probe. The sensor provides a response over a sulphate molarity range of 0 mol/l to 0.010 mol/l. And after being embedded inside the cement paste, the sensor still responds to sulphate. These features make this fluorescence-based fiber optic sulphate sensor potentially suited for in field and long-term monitoring of sulphate ions in the concrete structures, thereby enhancing structural health monitoring within the civil engineering sector.

1. INTRODUCTION

Concrete is a widely used construction material across the globe, and concrete structures constitutes a substantial portion of infrastructure. Usually, concrete structures are exposed to varies of impacts which may leads to reduction on the strength and service life[1]. Among these impacts, sulphate ions—stemming from the dissolution of gypsum, thiosulfate oxidation in the air, and the discharge of domestic will cause of concrete degradation[2]. Sulphate attack canl lead to concrete degradation like softening and decay of the concrete matrix or expansive cracking and other disruption associated with the formation of ettringite and other reaction products[3].

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For example, the formation of calcium sulphate dihydrate, leads to softening and loss of concrete strength [4].

$$Ca(OH)_2 + Na_2SO_4 \cdot 10H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH + 8H_2O \tag{1}$$

And the formation of calcium aluminate tri-sulphate, results in an increase in solid volume, and leads to expansion and cracking [4].

$$2(3CaO \cdot Al_2O_3 \cdot 12H_2O) + 3(Na_2SO_4 \cdot 10H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O + 2Al(OH)_3 + 6NaOH + 17H_2O \tag{2}$$

Therefore, a continuous monitoring of sulphate ion inside the concrete gives an indication for the early detection of problems influencing the concrete durability. Among various methods, fluorescence-based assays have widespread application due to the high sensitivity, nondestructive detection, and high spatiotemporal resolution. Fluorescence is the light emitted by an atom or molecule subsequent to the absorption of electromagnetic energy. The fluorescence arises from the transition of the excited species from its first excited electronic singlet level to its ground electronic level. Optical fiber sensors have advantages such as ease of miniaturization and integration, limited loss of light even over long distances, and low cost etc. Thus, in this work, a novel approach to monitor the sulphate ion inside the concrete structure is developed combining fluorescence-based assays and fiber optic sensor system method. Meanwhile, attention is also paid to the mechanical design of the sensor shell to ensure the sensors can be embedded inside the concrete safely.

2. EXPERIMENT AND METHODS

2.1 General

All reagents and solvents were of analytical or chemically pure grade. Scandium (III) oxide and morin hydrate were obtained from Aladdin. Hydrochloric acid, and ethanol were sourced from RCI Labscan. Sodium sulphate was purchased from Accuchem. The excitation-emission map was taken with FS5 Spectrofluorometer from Edinburgh Instruments.

2.2 Synthesis of the sulphate ion sensitive fluorescent material

Scandium solution: Scandium oxide (0.0959 g) and hydrochloric acid (50ml, 3 mol/l) were stirred in a 200 ml beaker with a thermostatic magnetic stirrer for 24 hours at 65 °C. The beaker is sealed with parafilm during heating. After cooling down, the scandium solution was diluted to 100 ml using a volumetric flask.

Morin solution: Morin solution was prepared by dissolving morin (0.1 g) in ethanol (100 ml).

Scandium-morin fluorescent complex: The complex was prepared by mixing scandium solution (2000 µl) and morin solution (4200 µl) together.

2.3 Sulphate sensing probe design and fabrication

After preparation of scandium-morin fluorescent complex, sulphate sensing probe was designed and fabricated with the following steps:

Preparation of the sulphate sensing film: Cellulose acetate powder (0.54 g) was dissolved with acetone (30 ml). Then, scandium-morin fluorescent complex solution (6200 µl) was added to the cellulose acetate acetone solution. Quartz pieces were cleaned with acetone and dried using compressed air. Once completely dry, scandium-morin fluorescent complex (80 µl) was pipetted onto the surface of the quartz pieces, which were then dried in fume cabinets. The sulphate sensing film was created by repeating this process four times.

Sensor housing fabrication: The sensor housing is fabricated using 3D printing technology. The lower part of the sensor housing features an O shape holder, which holds the filter membrane (20 µm) and quartz pieces with sensing film. The upper part of the sensor housing is a printed SMA connector. The probe's bottom allows the direct contact between the environment and the sensing film. All parts are protected by the waterproof glue.

2.4 Experimental set-up

The sensing probe was fabricated as described above, and the sensor system set-up is illustrated in Figure 1. The laser from a 10.08 mW LED (LSM-365A LED Light Source from Ocean Insight), emitting at a centre wavelength of 375 nm is coupled through a Y- type multimode VIS/NIR fibre with BX Jacket (Ocean Insight). The other end of the fibre coupler is connected to the sensor probe with a SMA connector. With the change of sulphate concentration, light emitted from the sensing element changes at the same time and the emitted light will be collected and guided through the other branch of the fibre coupler to an Ocean Optics USB2000+ spectrometer, with the output being displayed on a computer screen.

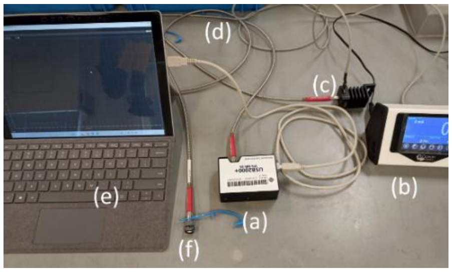


Figure 1. Setup of fluorescence-based fiber optic sensor system. (a) USB2000+ spectrum, (b) Ocean LED Single Channel Touchscreen Controller, (c) LSM-365A light source, (d)Y-type fiber, (e) Laptop with software, (f) sensor probe

2.5 Principle of sulphate concentration measurement based on fluorescence intensity

Morin (3,5,7,2′,4′-pentahydroxyflavone) is a well-known biologically active natural antioxidant existing widely in fruits, vegetables, and many herbs. It has two aromatic rings linked by an oxygen- containing heterocycle. Morin easily forms complexes by chelating metal ions due to the suitable arrangement of hydroxyl groups in the molecule [5]. For this reason, morin has this compound attracted attention as effective reagent for extraction and spectrophotometric determination of some metal ions [6].

According to Li [7], scandium ions formats complexes with morin. After the formation, the lowest singlet excited state of organic ligand Morin will change from n, π_1^* to π, π_1^* through intersystem crossing. The molecular structure will change from non-rigid to rigid, which makes the organic ligand of morin change from no fluorescence or weak fluorescence to strong fluorescence [8]. And compared with the weak coordination bonds formed between scandium ions and morin, the ionic bonds between sulfate ions and scandium ions are stronger. Therefore, sulfate ions can capture scandium ion from the scandium-morin fluorescence complex, and the structure of the complex is destroyed, leading to fluorescence quenching [9]. Thus, the scandium-morin fluorescent complex can be used to detect the sulphate ion.

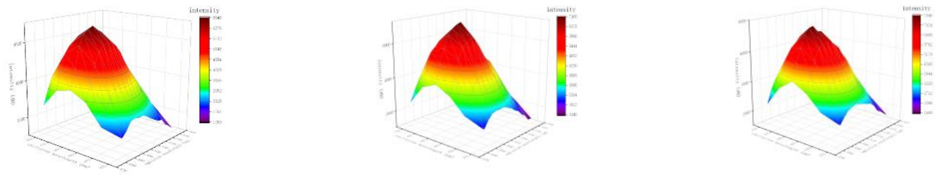
3. RESULTS AND DISCUSSION

3.1 Choice of concentration ratio

Six samples with varying concentration ratios of scandium and morin (as Table I shown) were tested to find the influence of concentration ratio of scandium and morin to the intensity of the emitted light. Samples were put inside the quartz tube, and the excitation-emission maps were taken with FS5 Spectrofluorometer from Edinburgh Instruments. The results, displayed in Figure 2 and Figure 3, reveal that the peak intensity value increases as the molar ratio rises from 1:4 to 2:1, and subsequently decreases when the molar ratio further increases from 2:1 to 3:1. Consequently, a molar ratio of 2:1 was chosen for subsequent tests.

TABLE I. SIX SAMPLES IN EXCIATION-EMISSION MAP TESTS

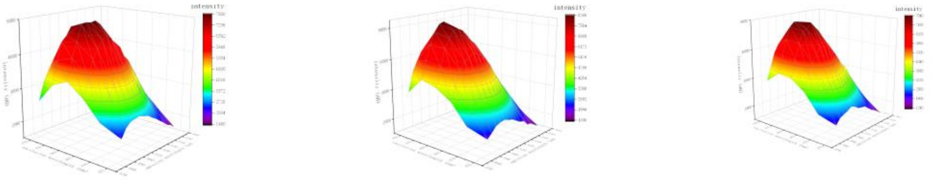
Water/μl	1372	1343	1282	1099	733	366
Scandium solution / μl	92	122	183	366	733	1099
Morin solution /μl	2040	2040	2040	2040	2040	2040
Sc : Morin molar ratio	1:4	1:3	1:2	1:1	2:1	3:1



Molar ratio 1:4

Molar ratio 1:3

Molar ratio 1:2



Molar ratio 1:1

Molar ratio 2:1

Molar ratio 3:1

Figure 2. Excitation-emission maps of 6 samples

3.2 Response of the scandium-morin fluorescent complex to the sulphate

The response of the scandium-morin fluorescent complex to sulphate was then investigated using a test setup similar to that described in section 2.4, with a probe devoid of sensing film. The results are depicted in Figure 4.

The intensity of the fluorescent light at 500.034 nm was shown in Figure 5. From Figure 5, we can see that the intensity of the scandium-morin fluorescent complex dropped down with the increase of sulphate molarity. And the ratio of initial fluorescence intensity (0) and the subsequent fluorescence intensity (n) has an approximately linear relationship when the sulphate molarity is below 0.01 mol/l.

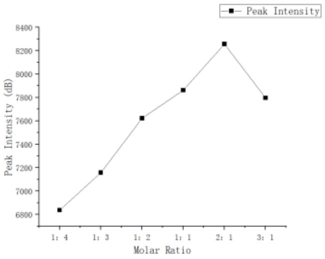
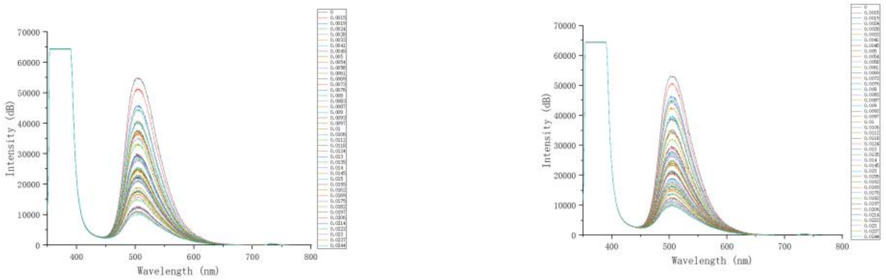


Figure 3. Peak value of the intensity in excitation-emission maps



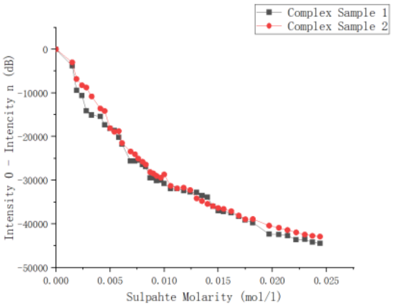
Sample 1

Sample 2

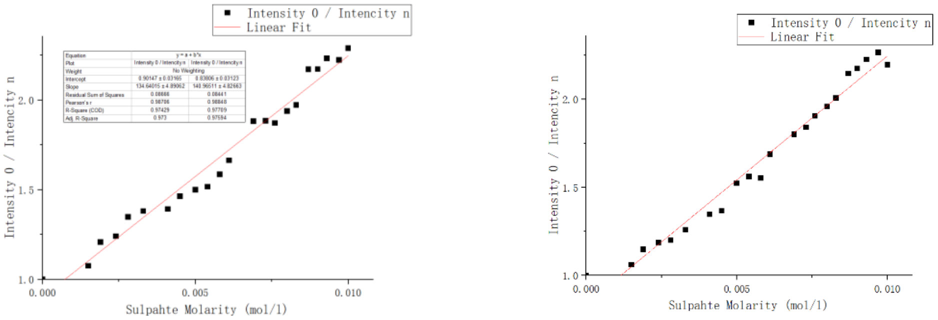
Figure 4 Response of the scandium-morin fluorescent complex to the sulphate

3.3 Response of the sulphate sensing probe to the sulphate

Following the investigation of the scandium-morin fluorescent complex's response to sulphate and the preparation of the sulphate sensing probe, the response of the sulphate sensing probe to the sulphate was tested with the setup shown in section 2.4. The results were shown in Figure 6 and Figure 7. Figure 6, demonstrates that the intensity of the sensing probe, after being converted from the scandium-morin fluorescent complex, still decreases with increasing sulphate molarity. And from Figure 7, the ratio of initial fluorescence intensity (0) and the subsequent fluorescence intensity (n) has a linear relationship when the sulphate molarity is below 0.01 mol/l. This indicates that the sulphate sensing probe works fine.



(a) Response of the scandium-morin fluorescent complex to the sulphate at 500.034 nm



(b) Linear fit of complex sample 1

(c) Linear fit of complex sample 2

Figure 5. Response of the scandium-morin fluorescent complex to the sulphate at 500.034 nm

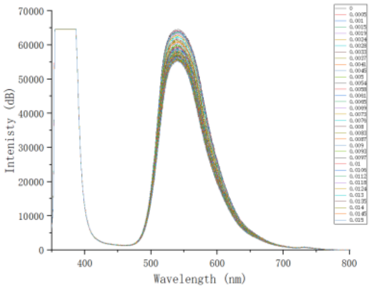
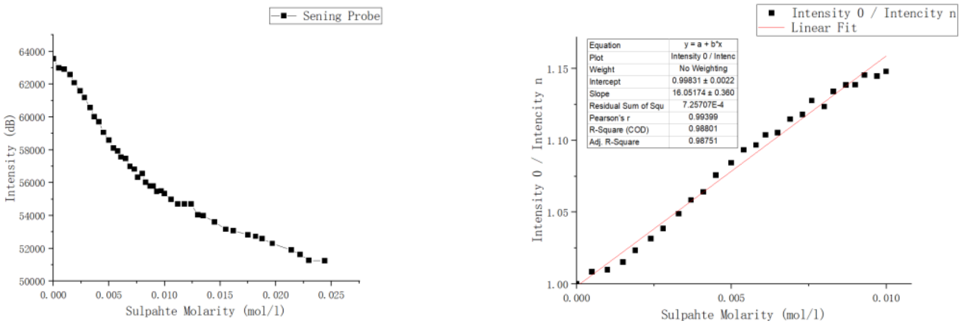


Figure 6. Results of the sulphate sensing probe to the sulphate



(a) Response of the sulphate sensing probe at 530.235 nm

(b) Linear fit of the response of sulphate sensing probe at 530.235 nm

Figure 7. Results of the sulphate sensing probe at 530.235 nm

3.4 Embedded test in lab

Subsequently, the sulphate sensing probe was embedded within cement paste to examine its functionality when embedded inside the cement. The test set up is shown in Figure 8. The sensing system is the same as the setup shown in 2.4 and the sulphate sensing probe is embedded inside the cement paste. The cement sample was put inside the sulphate solution after 7 days. The results are shown in Figure 9. From Figure 9 (a), we can see that the intensity of the sulphate sensing probe dropped significantly to around 17000 dB after the sulphate sensing probe being embedded inside the cement paste. Then the intensity keeps steady. In Figure 9 (b), time 0 denotes the moment when the cement sample containing the embedded sulphate sensing probe was placed in the sulphate solution, upon which the intensity decreased from around 17,000 to approximately 12,000. This suggests that the sulphate sensing film transferred from scandium-morin fluorescent complex works after being embedded inside the cement paste, and the sulphate sensing probe is effective in monitoring the sulphate inside the cement.

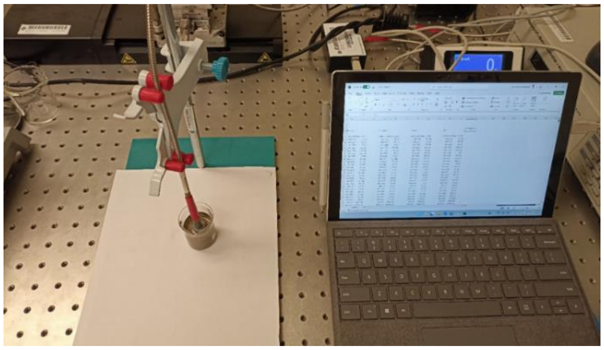
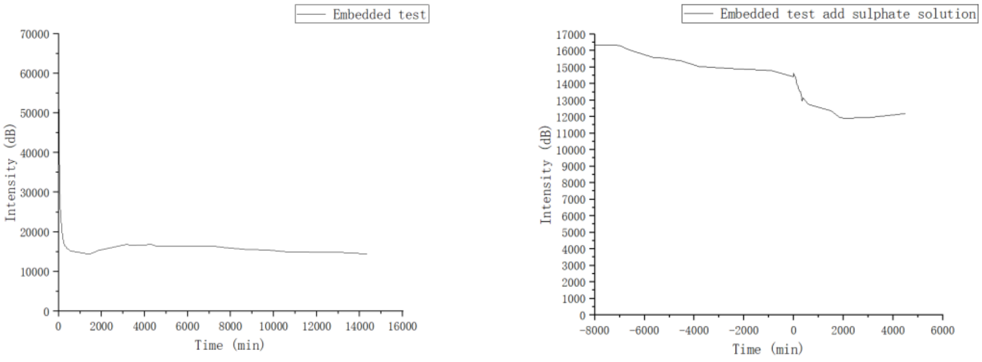


Figure 8. Embedded test setup



(a) Response of the embedded sulphate sensing probe

(b) Response of the embedded sulphate sensing probe after adding sulphate solution

Figure 9. Results of the embedded sulphate sensing probe

4. CONCLUSIONS AND FUTURE WORK

In this study, we have presented a fiber optic sensor system for embedded sulphate sensing. The sensing mechanism is based on the sulphate concentration change induced change in fluorescence intensity of the scandium-morin fluorescent complex which is transferred to a sensing film by cellulose acetate. The sensing film is between the quartz piece and the filter membrane (20 µm) and it is fixed at the end of a 3D printed housing which is designed to protect the sensing film when being embedded inside the concrete.

Laboratory tests demonstrate that the sulphate sensor is responsive to sulphate concentration below 0.025 mol/l and exhibiting a linear relationship between the initial fluorescence intensity (0) and the subsequent fluorescence intensity (n) for concentrations under 0.01 mol/l. Furthermore, the sulphate sensing probe remains responsive to sulphate even after being embedded within cement paste, which shows that the developed fluorescence-based fiber optic sulphate sensor might be suitable for long-term embedded sulphate sensing.

Ongoing work includes cross sensitivity tests which evaluate the influence of the chloride and pH to the sulphate sensor. Additionally, stability tests will be performed to ensure the sensor's long-term reliability and reproducibility, paving the way for successful field test applications of the sensor system.

5. REFERENCES

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