**Fundamental Study on the Development of Fiber Optic Sensor for Real-time Sensing of CaCO₃ Scale Formation in Geothermal Water**

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This study proposes an optical fiber sensor for calcium carbonate (CaCO₃) scale formation in water. The sensor is easily fabricated by removing the cladding of a multimode fiber to expose the core towards the surrounding medium in order to detect refractive index change. A variation of the transmittance response from the high refractive index of CaCO₃ which precipitated on the fiber core surface was observed. The proposed setup can be used to analyze the transmittance response over wide range of wavelength using white light as a source and also a spectroscopy detector. The curve of the transmittance percentage over time showed that a fiber core with 200 μm has higher sensitivity as compared to a fiber core with 400 μm. The findings from this study showed that the sensor detection region at near infrared (NIR) wavelengths showed better sensitivity than visible light (VIS) wavelengths. Field tests were conducted using natural geothermal water at Matsushiro, Japan in order to verify the performance of the proposed sensor. The optical response was successfully evaluated and the analytical results confirmed the capability of monitoring scale formation in a geothermal water environment.

**Keywords** Fiber optic sensor, scale, calcium carbonate, geothermal water, real-time sensing

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**Introduction**

One of the serious problems faced in the utilization of geothermal water is scale formation of inorganic salts, such as calcium carbonate, calcium fluoride, calcium sulfate or amorphous silica.1 Changes in the temperature and pressure affect the equilibrium, and hence lead to scale formation on the surface of wells found in equipment, such as wells, flow lines, valves, turbine and separators. As a result, the flow rate of ground water and the heat-exchange efficiency in the system can be decreased gradually from time to time. Due to this problem, a huge amount of cost is required for manpower-related maintenance and replacement, as well as to wash scales formed in the equipment.2 In order to prevent this problem, various techniques have been reported, such as the addition of organic phosphorus acid or ethylenediaminetetraacetic acid, a pH adjustment and ultrasonic irradiation.3–6 Therefore, evaluating the effectiveness of the present techniques concerning scale formation is important, especially since there is only limited research that has been conducted.

Typically, a direct visual inspection of the pipe’s inner surfaces condition is one of the techniques that have been introduced to evaluate scale formation. However, this is a labor-intensive method, and cannot be implemented for real-time monitoring purposes. In addition, inspecting the condition of pipe cannot be carried out while it is in use. Even though other techniques, such as turbidity measurement, gamma ray and ultrasonic have been suggested over the years to overcome the scaling phenomena,7–9 the problem still exists, and thus creating a potential impact on our economy.

Evanescent field spectroscopy is an extension of one of the established spectroscopic techniques, known as attenuated total reflection (ATR), which was used in the near-ultraviolet (UV), visible (VIS) and infrared (IR) spectral regions.10–14 This technique is based on the penetration of an evanescent wave through the sensing sample when the light that is traveling within waveguide undergoes total internal reflection. Over the past two decades, there has been an obvious trend towards the use of fiber optics with the ATR method offers a number of advantages when compared to the conventional ATR in terms of miniaturization, low cost
and real-time in situ remote monitoring. Apart from its ability to perform multiple chemical sensing, past studies have also shown that the fiber optic evanescent wave sensor can be operated in broad wavelength regions, such as UV, VIS, near infrared (NIR) and mid-IR. Smith et al. investigated the effects of an inhibitor and a dispersant on the CaCO₃ scale formation of the oil field using the standard ATR element. Several groups have reported on the fiber optic method for monitoring CaCO₃ precipitation by using an exposed core fiber optic, monochromatic laser light and detector. The detection principle was based on the percentage of total internal reflection within the fiber optic core, which was affected by the high refractive index of CaCO₃ scale formation on the core surface.

In this paper, a fundamental study was performed to develop an optimized fiber optic sensor for measuring the scale formation of CaCO₃ under the experimental conditions, and as well as to verify its performance in natural geothermal water. The sensor response was investigated based on optimization of the selected wavelength, fiber optic core diameter and also exposed core length. The scale formation was then examined by the saturation index (SI) of calcite. The implication of weight changes and surface coverage of scale was analyzed to understand the changes in the sensor responses. The scale formation of CaCO₃ salts from the natural geothermal water in Matsushiro, Japan was measured by the fiber optic sensor, as proposed in this study.

Experimental

Chemical reagents and materials

Sodium hydrogen carbonate, calcium chloride dihydrate and hydrochloric acid were purchased from Wako Pure Chemicals Industries, Ltd. The solutions were prepared by dissolving the above-mentioned chemicals in water. Two types of step index multimode optical fiber were used, which included FT200EMT and FT400EMT (Thorlabs, USA) with a 200 and 400 µm fused-silica core diameter, respectively. The refractive indices of both fiber cores were 1.444, which were surrounded by TEQSM™ polymer cladding with a refractive index of 1.443. The middle part of the fiber cladding was carefully rubbed and removed in order to expose part of the fiber core.

Sensing for CaCO₃ scale formation

The ELI-050J-OPT3077 (Mitsubishi Rayon, Japan) white light source device attached with a JCR12V-50WGAL (Ushio, Japan) halogen lamp was used to perform light coupling between a white-light source and an SA-100VRD VIS-NIR (Lambda Vision, Japan) spectroscopy detector through a fiber sensor. The fiber optic when exposed to a scale solution (I₀) by using a temperature controller placed under the watch glass. Transmittance values were acquired by recording the light intensity through the fiber optic when exposed to a scale solution (I₀), and after being exposed to scale formation as time proceeds (I). The transmittance of the fiber sensor was defined as T (%) = (I/I₀) × 100. The transmittance spectrum was measured continuously over the 300 to 1700 nm wavelength region.

Results and Discussion

Effect of the core size and wavelength

Table 1 Summary of the chemical properties of groundwater sampled in Matsushiro, Japan

| Temperature/°C | pH | Cl/mg L⁻¹ | ORP/mV | Na/mg L⁻¹ | K/mg L⁻¹ | Ca/mg L⁻¹ | Mg/mg L⁻¹ | SiO₂/mg L⁻¹ | HCO₃/mg L⁻¹ | SO₄/mg L⁻¹ | NO₃/mg L⁻¹ | Fe/mg L⁻¹ | Mn/mg L⁻¹ | Mg/mg L⁻¹ | ORP/mV |
|---------------|----|-----------|--------|-----------|----------|-----------|-----------|-------------|-------------|-------------|-------------|-----------|----------|-----------|---------|
| 24            | 6.7| 200       | 2300   | 4500      | 1100     | 310       | 8600      | 170         | 2.2         | 0.4         | 1.87       |           |          |           |         |

Measurement of scale weight and surface coverage

For measuring the weight changes on a formed scale, a glass slide with dimensions of 2 × 2.6 cm was immersed into the solution after mixing equivalent volumes of 80 mM of CaCl₂ and NaHCO₃. After a period of time, the glass slide was removed from the solutions, and its weight was measured one by one. The weight changes caused by the scale were obtained from the differences before and after immersing glass slides into the solution. In order to analyze the surface coverage of scale formation on the fiber core, the exposed fiber core was cut into a smaller portion which was then immersed into the calcium and carbonate solution. Scanning electron microscopy (SEM) was performed on the resulting surfaces of the fiber core with a TM-1000 Tabletop-Microscope (Hitachi, Japan). The produced SEM images were then used to analyze the coverage area as well as the surface coverage ratio.

Field study

In order to evaluate the effectiveness of the fiber sensor for monitoring scale formation, a field study was carried out in a geothermal water environment at Matsushiro, Nagano, Japan. The chemical parameters of the geothermal water are given in Table 1. Atomic absorption spectroscopy was used to determine the concentrations of Na and K, whereas Ca, Mg, Mn and total Fe were determined by using inductively coupled plasma atomic emission spectrometry. The gravimetry was used to measure SiO₂ and SO₄. Ion chromatography was used for measuring Cl⁻. Phenanthroline spectrophotometry was used to measure Fe(II), and Fe(III) was calculated by subtracting the Fe(II) from the total Fe. HCO₃ was measured by using a titration method. Three different electrodes were used to measure the pH, electrical conductivity (EC) and oxidation reduction potential (ORP).

A similar investigation conducted in the laboratory was repeated with the geothermal water. Different dilution levels of geothermal water samples (64, 94, and 100%) were prepared by adding tap water. The geothermal water was flowed through the fiber sensor fixed on the watch glass with tension applied to both ends. The concentration of the mixture was calculated from the electrical conductivity.

After each measurement, the scale formation on the fiber core surface was analyzed by investigating the X-ray diffraction (XRD). This analysis was performed using a Rigaku X-ray diffractometer operated at 40 kV and 40 mA with Cu Kα radiation.

Effect of the core size and wavelength

The effects of different parameters on the transmittance responses of fiber sensors were investigated. The transmittance
responses of both fibers with the 200 and 400 \( \mu \text{m} \) fiber core diameters were measured at wavelengths ranging from 300 to 1700 nm after both fiber sensors were immersed in the mixture of calcium and carbonate solution. The response, as shown in Fig. 1(a), indicates that the transmittances for both fiber sensors decreased to a constant value over time. In Fig. 1(b), it can be seen that broad lines were observed in the range from 1100 to 1700 nm. Furthermore, the transmittance response of the sensors showed better sensitivity at the NIR region, as compared to the VIS region. This might be related to the penetration depth of evanescent waves into the sample medium.

The refractive indices of a fused-silica core and calcium carbonate (calcite) are 1.455 and 1.652 at 700 nm, whereas at 1300 nm the indices are 1.444 and 1.638. The critical angle of the fiber, which is coated with TEQS cladding, is 87.9°, as calculated from Snell’s law. If scale formation is precipitated on the fiber core surface, the angle of refraction will be 61.6° at 700 nm and 61.8° at 1300 nm when the light is incident with the critical angle of the fiber. The Fresnel reflectivities, \( r_p^2 \), of the incident power for the p-polarized electric field and the reflectivities, \( r_s^2 \), for s-polarized electric field are given by:

\[
r_p^2 = \frac{(n_2 \cos \phi_1 - n_1 \cos \phi_2)^2}{(n_2 \cos \phi_1 + n_1 \cos \phi_2)^2} \quad (1)
\]

and

\[
r_s^2 = \frac{(n_1 \cos \phi_1 - n_2 \cos \phi_2)^2}{(n_1 \cos \phi_1 + n_2 \cos \phi_2)^2} \quad (2)
\]

where \( \phi_1 \) is the angle of incidence and \( \phi_2 \) is the transmission angle. The refractive indices of the media from which the light is incident is noted as \( n_1 \), and \( n_2 \) is the transmitted index. As calculated from the equation above, the reflectivities for the p-polarized and s-polarized electric field were 0.7063 and 0.7639 at a wavelength of 700 nm, whereas were 0.7065 and 0.7636 at 1300 nm. By comparison, the small deviations noticed in the reflectivities of both the VIS (700 nm) and NIR (1300 nm) regions suggest that the detection principle of the sensor does not solely depend on the loss of the propagated light caused by the conversion of the total internal reflection into external refraction due to the precipitation of calcium carbonate on the fiber core surface.

It is suggested that the loss of the evanescent light is another possible reason that allows detection of the fiber sensor, as shown in Fig. 2. Calcium carbonate occurs in three anhydrous crystalline polymorphs, such as cubic calcite, needle-like aragonite and spherical vaterite. Among them, calcite is the most thermodynamically stable, and a general polymorph is found when calcium carbonate precipitates from the geothermal water. When these crystals are precipitated on the surface of the fiber core, the area of the crystal surface that is in contact with the core surface will be limited. This is because of the different crystal polymorphs of calcium carbonate, which do not allow full contact with the cylindrical surface of the fiber core, and there might be some spaces present in between the fiber core and calcium carbonate. Due to this reason, an evanescent wave is generated at the spaces between the fiber core and the crystal surface. This evanescent wave is then absorbed by the crystal surface itself instead of reflecting back into the fiber core. Another factor that influences the detection of the fiber sensor is evanescent light loss. The evanescent wave will decay exponentially with the perpendicular distance from the surface. The penetration depth, \( d_p \), of the evanescent wave is directly proportional to the wavelength of the probing radiation, and is given by:

\[
d_p = \frac{\lambda}{2\pi n_2 \sin \phi_2}
\]
The results showed that the turbidity of the solution does not influence the sensor response after immersing the bare fiber into the mixture of calcium and carbonate solution. The transmittance obtained from the fiber sensor will decrease exponentially with the increment in the exposed fiber core length. It can then be said that the sensitivity response of fiber sensor in monitoring scale formation can be controlled by the length of the exposed fiber core.

**Effect on the saturation index of calcite**

To investigate the effect of calcite SI on the sensing performances, experiments were carried out by using various concentrations of calcium and carbonate solution. The geochemical modeling program PHREEQ C was used to evaluate the SI. The geochemical modeling program PHREEQ C was used to evaluate the SI.

The changes in the measured weight of the precipitated particle on the glass slides surface indicate that the precipitated particle weight is directly proportional to the immersion time of the glass slides. However, the tendency of increasing weight has no direct relation with the transmittance change monitored by fiber optic sensors. In addition, the surface coverage of the scale formed on the fiber core was observed through SEM, and was calculated based on the occupied area of the particles formed. The measurement results from Fig. 6 show that scale formation of the surface coverage on the fiber core was increasing up to a saturation point, after which the increment was no longer linear with time, even though the...

\[
d_d = \frac{\lambda}{\sin^2 \phi - \left( \frac{n_2}{n_1} \right)^2},
\]

where \( \lambda \) is the wavelength of light, and \( \phi \) is the angle of incidence; \( n_1 \) and \( n_2 \) are the refractive index of the core and the cladding, respectively. Therefore, it can be concluded that the NIR range has higher sensitivity for scale precipitation than the visible range due to the longer effective path length, as shown in Fig. 2(a).

On the other hand, the response of the fiber sensor will be affected by the core diameter as well. From the experimental results, the sensitivity response of the fiber sensor with a core diameter of 200 \( \mu m \) was higher than that of 400 \( \mu m \) in monitoring the calcium carbonate crystallization. This is caused by the increment in the number of ray reflections per unit length for a smaller fiber core diameter. As suggested by Potyrailo et al., the amount of absorption within the waveguide is directly proportional to the number of reflections.

The effect of turbidity on the fiber sensor performances was investigated by measuring the solution at every 10 min intervals after immersing the bare fiber into the mixture of calcium and carbonate solution. The results showed that the turbidity of the solution does not influence the sensor response.

**Effect of the exposed core length**

The effect of the exposed core length was tested by varying the length of the exposed fiber core. The transmittance responses of the fiber sensor towards the scale formation time with respect to the exposed fiber core length are as shown in Fig. 3. Given \( P_0 \) to be the transmitted power of the fiber in the absence of an absorbing fluid, the transmittance, \( P \), in its presence can then be represented as

\[
P = \frac{P_0}{\exp(-\gamma L)},
\]

where \( \gamma \) is the absorption coefficient of the fluid and \( L \) is the length of the exposed fiber core. As can be seen from Eq. (4), the transmittance obtained from the fiber sensor will decrease exponentially with the increment in the exposed fiber core length. It can then be said that the sensitivity response of fiber sensor in monitoring scale formation can be controlled by the length of the exposed fiber core.

**Fiber optic sensor characterization for scale formation**

The SEM images show scale particles in the form of sharp-edged calcite crystals that precipitated on the fiber core surface. By comparing Figs. 5(a) and 5(b), it can be clearly observed that the scale particles formed after 60 min were larger than those formed within 5 min. Spaces were observed between some of the precipitated particles and the fiber core surface, suggesting that the evanescent wave is absorbed by the scale.

However, when SI was 0.33, scale formation was not observed within 120 min.

![Fig. 3](image-url)  
**Fig. 3** Effect of the exposed core length on the transmittance responses monitored by a fiber sensor with 200 \( \mu m \) fiber core at a wavelength 1300 nm as a function of time after immersing the fiber in a solution containing 40 mM calcium and hydrogen carbonate. The changes in the measured weight of the precipitated particles and the fiber core surface, indicating that the evanescent wave is absorbed by the scale.

![Fig. 4](image-url)  
**Fig. 4** Transmittance responses monitored by fiber sensor with a 200 \( \mu m \) fiber core exposed length of 8 cm at a wavelength of 1300 nm as a function of time after immersing the fiber in a solution containing calcium and carbonate at different concentrations. The curves from top to bottom represent different saturation indices of calcite: 0.33 (2 mM), 1.0 (5 mM), 1.5 (10 mM), 1.8 (15 mM), 1.9 (17.5 mM), 2.0 (20 mM) and 2.4 (40 mM). The geochemical modeling program PHREEQ C was used to evaluate the SI.
weight and volume of CaCO₃ crystals are growing. This is due
to the limitation in the detectable area of the fiber core surface
which is in contact with the scale formed. It can be concluded
that the fiber sensor is sensitive to the surface coverage area of
the scale particles formed.

**Regeneration of the fiber optic sensor**

An ideal sensor should be able to be regenerated for continuous
monitoring or multiple uses. Figure 7 shows that the
transmittance returned to 100% after immersing the fiber sensor
in an acidic solution, which proves that the sensor can be
regenerated successfully.

**Field study**

The fiber sensor was tested in natural geothermal water that
consisted of a high concentration of calcium, carbonate, iron,
sodium and chloride at Matsushiro hot spring in Nagano, Japan
(Table 1). Based on the obtained water analysis, the magnitude
of the calculated SI was 1.9, and the scale formations of iron
hydroxide and calcite were observed in the geothermal water.

The results from the *in situ* monitoring of natural water
samples are shown in Fig. 8. A comparison between the
transmittance response of 200 and 400 μm fiber core diameters
showed that 200 μm core diameter tends to have a higher

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**Fig. 5** SEM images of the formed scale particles precipitated on 200 μm fiber core surface after
5 min (a) and 60 min (b) of an immersing time solution containing 40 mM calcium and hydrogen carbonate.

**Fig. 6** Transmittance responses of fiber sensor with a 200 μm fiber
core exposed length of 8 cm at a wavelength of 1300 nm with respect
to the surface coverage of calcium carbonate on the fiber core obtained
from SEM images over time after immersing in solution containing
40 mM calcium and hydrogen carbonate.

**Fig. 7** Transmittance response of the fiber sensor with respect to
scale formation measured by the fiber sensor with a 200 μm fiber core
exposed length of 8 cm at a wavelength 1300 nm after the regeneration
process by using a small volume of 1 M hydrochloric acid.

**Fig. 8** Transmittance of responses of fiber with a 200 and 400 μm
fiber core exposed length of 8 cm monitored at a wavelength 1300 nm
as a function of time after exposure of geothermal water (GW) and
diluted GW in Matsushiro, Japan. Saturation index of 100, 94 and
64% GW were 1.9, 1.8 and 1.4, respectively.
sensitivity. This observation was consistent with the results obtained from the laboratory experiment discussed earlier. However, the transmittance response rate of scale formation for a geothermal water field test took a longer time (300 min) to reach the same percentage (80% in this case), as compared with the laboratory experimental results, which only required 50 min. This deviation in time could be caused by the dissolved magnesium contained in the geothermal water. As for the laboratory experiment, the fiber core was immersed into a mixture that only contained a calcium and carbonate solution. On the contrary, in the case of the field study, natural geothermal water contained other highly dissolved salts, including Mg\textsuperscript{2+} (310 mg/L), which strongly inhibits the precipitation as well as the growth of calcite.\textsuperscript{40} Due to this reason, it is difficult for the scale to precipitate and grow on the fiber core surface in a short time.

Various concentration of geothermal water has been tested by fiber sensor with 200 μm fiber core. The results showed that the transmittance response at 100% concentration was faster than that of 94%. Besides that, in the case of geothermal water with 64% of concentration (SI = 1.4), the transmittance change observed was lower than the experimental result of SI = 1.5 obtained from Fig. 4. This could be explained by the presence of Mg\textsuperscript{2+} in the natural geothermal water. The XRD analysis of powder precipitated on the scale and fiber optics surface revealed calcite and iron oxide peaks. This observation clearly indicates that the fiber sensor is capable of monitoring scale formation in geothermal water environment.

Conclusions

The conducted studies in laboratory and field study conclude that the proposed sensor can be effectively used for monitoring CaCO\textsubscript{3} scale formation. The advantages of using the sensor proposed in this study are it can be used for real-time monitoring, ability to withstand harsh environmental conditions, small size, high sensitivity and cost effective. Furthermore, the use of a smaller fiber core diameter results in a much more sensitive detection. The key findings from this study clearly points out that the detection in NIR region can enhanced the sensitivity of the scale formation when compared to VIS region. The transmittance of fiber sensor corresponds to the surface coverage area during the scale formation on the fiber core. This sensor can be applied in geothermal environmental condition for remote and real-time monitoring of scale formation such as calcium fluoride, calcium sulfate or silica whereby the differences in refractive index between the scale and fiber optics contributes towards the detection sensitivity.

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