U-shaped plastic optical fiber sensor for scale deposition in hot spring water

Takuya Okazaki1 · Hisashi Kamio1 · Masaki Yoshioka1 · Akira Ueda2 · Hideki Kuramitz2 · Tomoaki Watanabe1

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Abstract
Fiber optic sensors for monitoring scale deposition in geothermal brine and hot spring water should be safe, easily fabricated, and readily disposable. These desired features already have been enhanced in plastic optical fibers (POFs) and U-shaped sensors for other applications. The present work reports a U-shaped POF sensor for CaCO3 scale deposition. The sensors were easily fabricated by thermally bending the bulk POF without removing the cladding. At the bend, the percentage of total internal reflection between the water and the POF surface is affected by the high refractive index of the CaCO3 deposit. The optical responses of the U-shaped sensor to CaCO3 formation were investigated in a mixture of calcium chloride dehydrate and sodium hydrogen carbonate using a white-light source and a spectroscopic detector. The sensor was responsive to CaCO3 formation on the sensor surface and was especially sensitive at small bending radii. The sensitivity was further enhanced by increasing the number of bends. Finally, the U-shaped POF sensor was applied to the monitoring of CaCO3 scale deposition in hot spring water sampled at Matsushiro, Japan.

Keywords Plastic optical fiber · U-shaped · Scale deposition · Hot spring water

Introduction
Scale formation due to the deposition of inorganic salts such as CaCO3, silica, or CaSO4 is a serious problem in equipment exposed to geothermal brine. Changes in pressure and temperature can change the solution equilibrium, inducing scale deposition on the surfaces of production and reinjection wells, brine pipelines, valves, turbines, and vapor–brine separators [1]. Such scale deposition gradually decreases the brine flow rate and the efficiency of the heat exchangers, incurring exorbitant costs associated with equipment maintenance, replacement of unrecoverable parts, and scale removal. The estimated overall cost of scale formation in the industrialized world is 26,850 million USD [2, 3].

Previously, we proposed fiber optic sensors that monitor scale deposition in geothermal brine and hot spring water using an exposed fused-silica fiber core, a halogen light, and a spectrometer [4–7]. The formation and growth of CaCO3 and silica scale is detected in real time as a change in the percentage of total internal reflection within the fiber optic core, which is influenced by the high refractive index of the scale formed on the fiber-core surface. The advantages of this type of sensor are real-time remote monitoring, heat resistance, small size, and cost-effectiveness. In geothermal fields, this sensor type has been applied in effectiveness evaluations of chemical scale inhibitors and electromagnetic field treatments against scale formation. However, geothermal-field applications of this sensor are inhibited by the high fragility of the 200-µm diameter fused-silica core of the exposed fiber optic cable. In our previous case, the polymer cladding of the fiber optic was carefully rubbed and removed with an acetone-soaked tissue. This process requires specialized skills and the residual cladding directly affects the sensing results.

Recently, various types of chemical and bio-sensors based on plastic optical fibers (POF) have been proposed [8]. These sensors can be D-shaped [9–11], taped [12, 13], U-shaped [14–20] or uncladded [21, 22]. As POF is much more flexible than silica fiber optic, it is safe and easily fabricated and...
operated. To allow the light transmitted through the fiber to enter the external sample, the POF cladding is removed or the core modes are coupled to the cladding modes. POF is suitably flexible for forming these types of sensors. U-shaped POF sensors are especially recognized for their excellent handling properties and have been used as chemical and bio-sensors [8]. In most cases, the fiber cladding is removed by polishing or chemical etching in ethyl acetate [14–18, 20]. Removing the polymer cladding from the polymer core is a very delicate operation. Moreover, ethyl acetate is a relatively hazardous chemical. Werneck et al. [14] reported a U-shaped POF biosensor that detects *Escherichia coli* without requiring cladding removal. They explained that the cladding supports a few propagating modes at its bend. At the cladding–analyte interface is another critical angle that guides all cladding modes hitting this interface at higher angles. These cladded U-shaped POF sensors can be fabricated easily without requiring delicate polishing [23] or chemical removal of the cladding. In addition, Zhong et al. [9] reported that the transmittance of a D-shaped POF is affected by the absorption of water molecules into a POF core made of poly methyl methacrylate (PMMA). The fluoropolymer cladding can improve the chemical stability of the sensor.

The present study proposes a U-shaped POF sensor for real-time monitoring of scale deposition in hot spring water. The U-shaped sensor can be inserted easily into hot spring water or geothermal brine in the field. The cladding modes of the sensor, which are coupled from the core modes at the bend point, are prevented from undergoing total internal reflection by the high refractive index of scale, and are consequently leaked from the fiber. As scale sensors are disposed after use, they must be easily fabricated in large numbers. Here, the sensors were simply fabricated by thermally processing the inexpensive POF into a U-shape without removing its cladding. The optical response of the sensor to CaCO₃ surface deposition was investigated in water. The number of bends in the POF was optimized to further enhance the sensor sensitivity. The effect of bend number on the detection sensitivity was evaluated using ethyl violet (a cation dye). Finally, the sensor was applied to CaCO₃ scale deposition in hot spring water sampled in Matsushiro (Nagano, Japan). This is the first report on POF sensors application to sense geothermal scale, which are easy to process and cost effective, for scale deposition in hot spring water.

### Experimental

#### Chemical and materials

Sodium hydrogen carbonate, calcium chloride dehydrate, and sodium hydroxide were purchased from Wako Pure Chemical Industries, Ltd. Solutions of these compounds were prepared by dissolution in water. The fiber was a PGS-FB250 (TORAY, Japan) step-index multimode POF with a 240-µm-diameter PMMA core (refractive index [RI] = 1.49) and a 10-µm-diameter fluoropolymer cladding (RI = 1.41). The center of the POF was bent to form a U-shape, as shown in Fig. S1 (a). The POF was heated to 100 °C in an oven before use, then pulled around a metal wire and heated to approximately 100 °C by a heat gun. POFs with three and five bends were fabricated using two wires [Fig. S1 (b)] and fixed in a sleeve to form a tube [Fig. S1 (c)]. The bending radius of the U-shaped sensors was determined from images captured by a microscopic digital camera (WG-5, RICOH, Japan). The POF sensor was connected to a halogen white-light source and a spectroscopic detector (Color compass MF, AT system, Japan).

#### Evaluation of CaCO₃ formation

Immediately after mixing equivalent volumes of 120 mM CaCl₂·2H₂O and 120 mM NaHCO₃ solutions, the sensor regions of the POFs were immersed into 100 mL of the resultant solution. Because the formation of CaCO₃ in water in the laboratory is affected by various external conditions such as temperature and the carbonate concentration in water, the bending radius and bend number were investigated using several spectrometers and light sources, and tests of each sensor were performed in the same sample solution. Hot spring water containing iron (II), calcium and carbonate was sampled in Matsushiro (Nagano, Japan) in September of 2020. The temperature, pH, and electrical conductivity of the hot spring water were 45.1 °C, 6.74 and 2.64 Sm⁻¹, respectively. The hot spring water was placed in an airless bottle and immediately refrigerated at 4 °C. The chemical parameters of the hot spring water will be close to those of our previous measurement [7]. For the CaCO₃ test, 90 mL of the hot spring water with the immersed POF sensors was heated to 50 °C within 7 min.

The sensor transmittance was calculated as $T = (I/I₀)$, where $I$ is the optical intensity through the sensor and $I₀$ is the initial intensity. The exposure time of the spectroscopic detector was set at 10–20 ms.

#### Evaluation of ethyl violet

The POF sensors were immersed in approximately 10 mL of 10 µM ethyl violet solution and the absorbances after 5 min were used as the measurement values.
Results and discussion

Effect of temperature

First, the effect of temperature on a POF (PGS-FB250) was investigated. In this experiment, the unprocessed POF, before being processed into a U-shape, was connected to the light source and detector and a section of the POF (approximately 5 cm) was alternately immersed in water at 80 °C and 25 °C (Fig. S2). After immersion in 80 °C water, the transmittance immediately decreased to ca. 80% and then increased to 93%. Thereafter, a temperature change altered the transmittance by only a few percent. Zhong et al. [9] reported that the transmittance is reduced and stabilized once the PMMA of POF has reached its glass-transition temperature and the molecules have spontaneously rearranged. In the present study, the transmittance change was small after the first heating, so the POF in bulk was heated once and then fabricated into the U-shaped sensor. Such an annealing process has been often used for Bragg grating sensors based on POF [24, 25], and their effects have also been discussed [26].

Effect of bending radius

Figure 1a shows the transmittance changes due to CaCO₃ formation on the U-shaped POF sensors with different bending radii (0.24, 0.33, and 0.76 mm) and without bending. The sensors were fabricated using metal wires with different diameters. The 250-μm-diameter POF (PGS-FB250) could not reach a bending radius of less than 0.24 mm by this method. The transmittances of all bent sensors (regardless of their bending radius) decreased after CaCO₃ formation, indicating that CaCO₃ formation on the cladding surface of the POF can be detected using the light passing through the cladding at the bending point. For the sensor without bending, there was no change in transmittance. The smaller is the bending radius of the sensor, the larger is the change in transmittance and the higher is the sensitivity. This tendency agrees with the simulation and experimental results of Rodrigues et al. and Teng et al., who reported that the sensitivity of fibers with diameters around 250 μm increases with decreasing bend radius [15, 17]. The sensitivity enhancement was slightly more pronounced in the 0.33–0.24 mm range of bending radii (Fig. 1b).

Effect of bend number

The developed sensor monitors scale deposition from the light-intensity changes through the optical fiber. To improve the sensitivity, the response to CaCO₃ formation was evaluated in sensors with different numbers of bends (Fig. 2). In this experiment, the bend number was set to 1, 3, and 5 for easy insertion into the water sample. The transmittance change increased by increasing the number of bends. The absorbances calculated from the transmittance changes due to CaCO₃ formation were linearly related to the sensing area of the sensor [4]. When the bend number increased from 1 to 3 and 1 to 5, the absorbance increased by a factor of 1.8 and 2.4, respectively (Fig. 2b). This disagreement between the factor and the bend number indicates that not all of the light passing through the POF is used for sensing CaCO₃ formation. The relative standard deviations measured using three fabricated sensors with 1, 3, and 5 bends were 5.7%, 8.4%, and 17%, respectively, at 80 min after the CaCO₃ formation.

Fig. 1 a Transmittance responses (at 600 nm) of U-shaped POF sensors with different bending radii to CaCO₃ formation; b relationship between transmittance at 100 min and bending radius. Results and error bars are the means and standard deviations, respectively, of three replicates (n = 3)
formation. As mentioned above, the sensitivity of the sensors was affected by the bend radius. The increase in the relative standard deviations with an increase in the number of bends can be attributed to the increased shape errors due to hand processing.

Figure S3 (a) and (b) shows the scanning electron microscopy (SEM) images obtained after 10 min of CaCO₃ crystallization on the surface of the POF. At that immersion time, the sensor transmittances with 1, 3, and 5 bends were 0.81, 0.70, and 0.64, respectively. The surface coverage was 29% [Fig. S3 (b)]. Fiber optic sensors are sensitive to the surface coverage area of the CaCO₃ particles [4]. When the silica-core fiber sensor was 29% covered with CaCO₃, the transmittance was approximately 0.3. Therefore, a POF sensor can be expected to be less sensitive than the exposed silica-core sensor to CaCO₃ deposition per sensor surface area.

To confirm the relationship between the response and sensing area of the sensor, spectrophotometry (which is based on the evanescent waves generated on the fiber surface) was performed with a cationic dye (ethyl violet). Figure 3 shows the absorption spectra of POF sensors with 1, 3, and 5 bends after 5 min' immersion in 10 µM ethyl violet solution. This spectrophotometric analysis uses the absorption of evanescent waves generated at the interface between the fiber surface and the external medium by the total internal reflection of the light transmitted through the fiber. The equation of evanescent-wave absorption is based on Beer's law and is given by

$$A = \frac{4}{3} \sqrt{\frac{\lambda}{2\pi r n^2_{\text{core}} - n^2_{\text{cladd}}}} \frac{\alpha C L}{2.303},$$  

where $C$ is the concentration of the external medium, $\lambda$ is the wavelength, $\alpha$ is the absorption coefficient, $r$ is the radius of the fiber core, $L$ is the length of the exposed fiber core, and $n_{\text{core}}$ and $n_{\text{cladd}}$ are the refractive indices of the core and cladding, respectively [27]. Note that the absorbance of the sensor is linearly related to the exposed core length, i.e., to the sensing area. All sensors clearly obtained the absorption spectrum of ethyl violet (Fig. 3). The absorbance increased as the number of bends increased. This result is consistent with the result of CaCO₃ formation, confirming that the bends caused the light transmitted through the POF to reach the sensor–sample interface, where total internal reflection occurred.

Ethyl violet exhibits an absorption peak at approximately 600 nm in general spectrophotometry; however, the fiber sensor observed a maximum absorption at 550 nm, consistent with that of the silica core sensor [28]. The differences in peak wavelength between the two methods might be explained by adsorption of ethyl violet on the fiber surface. Luo et al. reported that monomers and dimers of
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Ethyl violet show characteristic absorption peaks at 595 and 556 nm, respectively [29]. Therefore, the fiber sensor may be more sensitive to ethyl violet dimers than general spectrophotometry.

The absorbance of the five-bend sensor in 10 µM ethyl violet was around 0.2, close to that of a silica fiber with an 8-cm-long exposed core [28]. The sensing areas of the present sensors with millimeter-scale bending radii are very much smaller than that of an 8-cm fiber. The observed absorbances can be explained by the stronger adsorption of ethyl violet on the surface of a fluoropolymer cladding sensor than a silica sensor. Therefore, the U-shaped POF sensor can be applied to sensitive determinations of surfactants or dyes based on ion-associated adsorption [28, 30, 31].

Application to hot spring water

Finally, the U-shaped POF sensor was tested in natural hot spring water from Matsuhiro (Japan), which contains high concentrations of iron (II), calcium and carbonate. The elemental ratios of the scale from this hot spring water were 20.6% carbon, 14.1% oxygen, 6.7 aluminum, 1.5% Si, 15% calcium and 40% iron (SEM-energy dispersive X-ray spectroscopy results). The sample (90 mL of hot spring water) was kept at 4 °C and heated to 50 °C in 7 min by a mantle heater, while the sensor started the measurements. As the temperature increased, the formation of CaCO$_3$ is accelerated. Figure 4a shows the transmittance changes recorded by the one- and three-bend sensors in hot spring water. After reaching 50 °C, the scale deposition was clearly monitored by both sensors but the three-bend sensor showed higher sensitivity. In addition, the scale deposition on the sensor surface and light leakage from the deposits were observed in photographs taken before and after the experiment (see the three-bend sensor before (left) and after (right) CaCO$_3$ scale deposition in the hot spring water sample).

Conclusions

We proposed a U-shaped POF sensor for the detection of scale deposition in hot spring water. The sensor was easily fabricated by thermally bending an inexpensive POF into a U-shape without removing its cladding. The sensor responded to CaCO$_3$ formation and showed higher sensitivity at a smaller bend radius than for larger ones. The sensitivity was further enhanced by increasing the number of bends. This fact was confirmed by spectrophotometry using ethyl violet, which is based on evanescent waves. The sensor was successfully applied to the detection of CaCO$_3$ deposition in hot spring water sampled at Matsushiro (Japan). This U-shaped sensor can be easily inserted into the test sample. POFs are inexpensive and can be incorporated into a cheap and simple sensor system with light-emitting diode light sources and a diode detector.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest The authors declare no conflict of interest.
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