Fiber Optic Sensor for Real-Time Sensing of Silica Scale Formation in Geothermal Water

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We present a novel fiber optic sensor for real-time sensing of silica scale formation in geothermal water. The sensor is fabricated by removing the cladding of a multimode fiber to expose the core to detect the scale-formation-induced refractive index change. A simple experimental setup was constructed to measure the transmittance response using white light as a source and a spectroscopy detector. A field test was performed on geothermal water containing 980 mg/L dissolved silica at 93 °C in Sumikawa Geothermal Power Plant, Japan. The transmittance response of the fiber sensor decreased due to the formation of silica scale on the fiber core from geothermal water. An application of this sensor in the evaluation of scale inhibitors was demonstrated. In geothermal water containing a pH modifier, the change of transmittance response decreased with pH decrease. The effectiveness of a polyelectrolyte inhibitor in prevention of silica scale formation was easily detectable using the fiber sensor in geothermal water.

One of the serious problems with the use of geothermal water is the scale formation of inorganic salts such as calcium carbonate (CaCO₃), amorphous silica, or calcium sulfate. Changes in temperature and pressure influence the equilibrium by inducing scale formation on the wall surface of wells, flow lines, valves, turbines, and separators. Such scale formation results in a gradual decrease of water flow rate and heat-exchange efficiency of a given system. This results in exorbitant operating costs for maintenance, replacement, and removal of scale from equipment. The estimated cost spent to tackle scale formation problem in the industrialized world is estimated to be 26,850 million USD.

Numerous techniques have been reported for prevention of CaCO₃ scale formation, such as the addition of chemical inhibitors including polyelectrolytes, organophosphates, ethylenediaminetetraaceta, metal ions, and nanoparticles and other techniques involving surface modification of equipment, pH modification, and ultrasonic or electromagnetic irradiation. On the other hand, although silica scale is observed in geothermal plants in equal or greater frequencies than CaCO₃ scale, there are significantly fewer reports in the literature concerning silica scale prevention techniques; these techniques include the addition of polyelectrolytes, borates, chelating reagents, and dendrimers, and pH modification. The applications of these methods in geothermal fields are also limited. One of the reasons is that the effectiveness of these techniques for silica scale prevention has not been identified due to the complex mechanism of silica scaling. In addition, it has been reported that silica scaling is exacerbated by the addition of a slightly excess amount of inhibitors, which causes the acceleration of agglomeration or precipitation of silica. Therefore, the effectiveness of the silica scale prevention techniques should be carefully evaluated to understand the behavior of silica scaling and to recognize potential techniques that could further contribute to overcoming this problem.

Table 1 shows the methods for monitoring silica scale formation reported in literature on scale prevention or control. Most of these methods can be classified as weighing the deposited scale, chemical analysis of soluble silicate, and flow rate monitoring in test equipment. The weighing methods provide the amount of scale precipitated on experimental equipment. However, such methods require a long deposition time to detect the change in the scale amount obtained by a balance. The chemical analysis of soluble silicate with molybdate colorimetry is useful in the investigation of the polymerization behavior of silicates. Nevertheless, this method...
Geothermal Power Plant, Japan. As shown in Fig. 2(A), the transmittance response decreased due to scale for-
to detect not only CaCO₃ but also silica scale formed in geothermal water. In our previous work, we proposed an optical fiber sensor
exposed core fiber and monochromatic laser light37–40. The detection principle of this sensor was based on the percentage of total internal reflection
rate monitoring methods enable a direct evaluation of the effect of scaling on flow properties18, 19. Such methods
is an indirect evaluation of scale formation, time consuming, and complicated for continuous monitoring. Flow rate monitoring methods enable a direct evaluation of the effect of scaling on flow properties18, 19. Such methods can easily allow continuous monitoring of the flow rate and hence the scale formation in equipment. However, they require design and fabrication of experimental flow systems and it takes a long time (a few days to a week) for scale formation to affect the flow rate. Even though other techniques, such as turbidity measurement, gamma ray, and ultrasonic, have been suggested over the years to monitor the scaling phenomena, the problem still exists, and thus creates a potential impact on our economy29–31.

Over the past two decades, there has been a clear trend toward the use of fiber optics in the detection of chem-
cal. Several groups have reported the fiber optic method for monitoring CaCO₃ precipitation by using an exposed core fiber and monochromatic laser light32–40. In our previous work, we proposed an optical fiber sensor that uses an exposed core fiber, white light, and a spectroscopy detector for monitoring CaCO₃ scale formation in geothermal water41. The detection principle of this sensor was based on the percentage of total internal reflection within the fiber optic core, which is affected by the high refractive index of CaCO₃ scale formed on the surface of an exposed core. The advantages of this sensor include high sensitivity, real-time remote monitoring, heat resistance, small size, ease of handling, and cost effectiveness. Moreover, the design and fabrication of a specific experimental system mentioned above are not required for geothermal scaling monitoring.

In this study, a novel fiber optic sensor for silica scale formation was developed under experimental conditions. The field test was conducted at Sumikawa Geothermal Power Plant to analyze the performance of the sensor. The novelty of this study is the development of a sensor for monitoring silica scale formation in geothermal water in real time. To the best of our knowledge, this is the first reported case of a sensor that can evaluate the effectiveness of scale inhibitor. Real-time monitoring is necessary because the reaction of scale formation in geo-

| Monitoring methods | Situation | Scale | Scale inhibitor or controller | Measurement period | Reference |
|--------------------|-----------|------|------------------------------|-------------------|----------|
| Weighing the scale collected in spools | Laboratory and geothermal field | Silica | Mixed chemical inhibitor | 48 h | 25, 27 |
| Measurement of monomeric silica in water by molybdate colorimetry | Laboratory | Aluminum silicate | pH modification Chelating reagent | 4 h | 13 |
| Weighing the scale collected in spools | Laboratory and geothermal field | Aluminum silicate | Chelating reagent | 48 h | 14 |
| Monitoring the flow rate through a column packed with alumina beads | Geothermal field | Silica | pH modification | 150 h | 18 |
| Monitoring the flow rate through a fluidized-bed reactor | Geothermal field | Silica | pH modification Chemical impurities | 48 h | 19 |
| pH measurement | Geothermal field | Silica | pH modification with biochemical reactor | 30 days | 20 |
| Measurement of monomeric silica in water by molybdate colorimetry | Geothermal field | Silica | pH modification | 200 days | 21 |
| Weighing the scale deposited on stainless steel rods | Geothermal field | Metal silicate | Commercial inhibitors | 24 h | 28 |
| Measurement of silica in water by molybdate colorimetry | Cooling water | Silica | Dendrimers | 72 h | 16, 17 |
| Weighing the scale collected in column | Cooling water | Silica | Polyelectrolyte | 10 days | 12 |
| Measurement of monomeric silica in water | Reverse osmosis treatment | Silica | Chelating reagent | 9 h | 15 |

Table 1. Examples of methods of monitoring silica scale formation in the literature on scale prevention or control.

Results

Laboratory study. Transmittance responses were measured at wavelengths ranging from 500 to 1700 nm after the fiber sensor was immersed in a silicate solution (1000 mg/L as SiO₂) at 90°C. The transmittance decreased over time, as shown in Fig. 1(A). Broad lines were observed in the range from 500 to 850 nm, as indicated in Fig. 1(B). The transmittance response of the sensor showed slightly better sensitivity in the near-infrared region than in the visible region. This tendency is similar to the results of our previous measurement for CaCO₃ scale, which has a higher refractive index than the quartz fiber core41. The result indicates that the sensor is able to detect not only CaCO₃ but also silica scale formed in geothermal water.

Field study. To evaluate the effectiveness of the fiber sensor in monitoring silica scale formation, a field test was performed on geothermal water containing 980 mg/L dissolved silica as SiO₂ at 93 °C in Sumikawa Geothermal Power Plant, Japan. As shown in Fig. 2(A), the transmittance response decreased due to scale formation in geothermal water. The sensor detection region at visible wavelengths showed better sensitivity than at
near-infrared wavelengths. This result is in disagreement with the laboratory result. Philip-Chandy et al. reported that transmitted light decreases as a function of increasing refractive index of the cladding when the cladding has a lower refractive index than the fiber core. The higher sensitivity at visible wavelengths could be explained by wavelength dependence of the refractive index of silica formed on the quartz fiber core: the refractive index of silica increases as the wavelength decreases. Moreover, it seems that the difference in results between laboratory and field tests could be related to the slight difference in purity between pure SiO$_2$ formed in the laboratory test and silica scale precipitated in geothermal water in the field test. The transmittance spectrum in the field test showed broad lines in agreement with the laboratory result. After the field test, the scale was analyzed by XRD measurement, which showed only the peak of silica.

**Effect of exposed core length.** The effect of exposed core length was examined by varying the length of exposed fiber core in geothermal water, as shown in Fig. 3. The transmittance value obtained from the sensor increased with increase in the exposed fiber core length. In this figure, the tendency of decreasing transmittance in all results is divided into two steps, the initial rapid change and the subsequent gradual change. It seems that the first step is due to precipitation of silica scale on the fiber core and the second step is caused by growth of silica covering the fiber core. The slope of the transmittance decline in the second step also depended on the exposed fiber core length. This might be related to the total amount of scale precipitated on the fiber core.

**Evaluation of pH modifier.** The use of a pH modifier as a silica scale inhibitor was examined in geothermal water at Sumikawa Geothermal Power Plant. In these tests, the exposed core length of 24 cm was used, which has the highest sensitivity as in the previous results. Changes in transmittance with time at different concentrations of the pH modifier in geothermal water are shown in Fig. 4. The change in transmittance decreased with decreasing pH in geothermal water. It is well known that silica scale deposition is affected by the solution pH because the
solubility of silica scale increases with a decrease in pH over a pH range of 4–9. Our results agreed with this known tendency. It is shown that the sensor can clearly measure the effect of pH change on silica scale formation within 6 h.

Evaluation of polycarboxylic acid inhibitor. Figure 5 shows the transmittance response of the fiber optic sensor in geothermal water containing a polycarboxylic acid inhibitor. The transmittance change at an inhibitor concentration of 1 mg/L was clearly smaller than that of 0 mg/L. This result shows that the sensor could detect the effect of the scale inhibitor in geothermal water within a few hours. On the other hand, the rate of transmittance decrease at an inhibitor concentration of 2 mg/L was larger than that at 1 mg/L. Gallup reported that higher concentrations of an organic inhibitor at the ppm level enhanced scale formation due to flocculation or agglomeration of silica. In this experiment, the effectiveness of the organic inhibitor for the inhibition of scale formation reduced at a concentration of 2 mg/L. The key finding from the experiment is that the fiber optic sensor could easily detect the small differences in the inhibitor effectiveness during a short time (less than 7 h) in geothermal field. This rapid and continuous observation of scale formation will contribute to the development of techniques for silica scale prevention in geothermal water.

Discussion
To measure the amount of scale formed on the fiber sensor, the scale thickness was measured by vertical scanning interferometry using quartz plates immersed in geothermal water, as shown in Table 2. The scale thickness linearly increased with the deposition time in geothermal water, and the average growth rate of the scale was 15.5 nm/h. By using this value, the rates of increase in the volume of scale formed on the exposed fiber core were calculated. For a 200-μm-diameter fiber with lengths of 8, 16, and 24 cm, the scale volume growth rates are $0.80 \times 10^{-3}$, $1.59 \times 10^{-3}$, and $2.39 \times 10^{-3}$ mm$^3$/h, respectively. The distances between these values are in close
agreement with absorbance increment as a function of time, which is calculated from the transmittance responses in Fig. 3. From these results, the relationship between the absorbance of the fiber optic sensor and the weight of scale formed on the fiber core can be represented as

\[ A = -\log\left(\frac{I}{I_0}\right) = 9.64m + A_i \]

where \( A \) is the sensor absorbance, and \( I_0 \) and \( I \) are the light intensity before and after scale formation, respectively, \( m \) is the weight of scale formed on the fiber core (calculated using quartz density = 2.635)\(^4\), and \( A_i \) is the small change in absorbance in the first step mentioned above. From the equation, this sensor is sensitive to the weight of scale formed on the fiber core and its sensitivity can be increased by increasing the exposed fiber core length, as this increases the total amount of scale. Therefore, the sensitivity and working time of the fiber sensor for monitoring silica scale in geothermal water can be easily controlled by the length of the exposed fiber core. Moreover, the results showed that this sensor can detect a continuous change of scale weight at the 1\( \mu \)g level, whereas the typical weighing technique for silica scale monitoring uses balances with a precision of 0.1 mg.

### Methods

**Chemical reagents and materials.** Sodium metasilicate nonahydrate and sulfuric acid was purchased from Wako Pure Chemicals Industries (Japan). The pH modifier consisting of maleic acid and polyacrylate was obtained from Techno Office Japan. The polycarboxylic acid inhibitor was supplied by BWA Water Additives Japan Limited.

A step-index multimode optical fiber (FT200EMT; Thorlabs, USA) with a 200-\( \mu \)m-diameter fused silica core was used. The fiber core has a refractive index of 1.451, and it is surrounded by TEQSTM polymer cladding with a refractive index of 1.392 at 1020 nm. The fiber cladding was carefully removed from the middle of the fiber by rubbing to expose the fiber core.

A white light source (ELI-050J-OPT3077; Mitsubishi Rayon, Japan) attached with a halogen lamp (JCR12V-50WGAL; Ushio, Japan) was used to perform light coupling between the white light source and a spectroscopy detector (SA-100VRD VIS-NIR; Lambda Vision, Japan) through the fiber sensor. Sensor transmittance values were acquired by recording the light intensity through the fiber before exposure to scale formation \( (I_0) \) and the intensity after exposure to scale formation as time proceeds \( (I) \). Sensor transmittance in the fiber sensor was defined as \( T (\%) = \frac{I}{I_0} \times 100 \). It is confirmed that the variation of the transmittance obtained from the system that utilized an unprocessed fiber optic was less than 1% over a time span of 10 h. A stabilized power supply was used during the field experiments. However, if a stable transmittance cannot be obtained, then an optical switch of 1 × 4 for multipoint monitoring was applied. The unprocessed fiber is connected to one of the ports at the optical switch and is used as a reference for optical intensity.

### Table 2.

| Deposition time (h) | Scale thickness (\( \mu \)m) |
|--------------------|-----------------|
| 22.8               | 0.36 ± 0.01     |
| 46.8               | 0.63 ± 0.02     |
| 70.8               | 1.14 ± 0.03     |
| 118.8              | 2.08 ± 0.02     |
| 166.8              | 2.45 ± 0.27     |

Table 2. Scale thickness on quartz plates in geothermal water (n = 3).

![Figure 5. Effect of the polycarboxylic acid inhibitor on the scale formation monitored by the fiber optic sensor. Exposed core length: 24 cm; wavelength: 600 nm; inhibitor concentration: 1 mg/L (red line), 2 mg/L (yellow line), and 0 mg/L (green line).](image-url)
and total Fe concentrations were determined using inductively coupled plasma atomic emission spectrometry. Atomic absorption spectroscopy was used to determine the concentration of Na and K, whereas Ca, Mg, Mn, Al, and total Fe concentrations were determined using inductively coupled plasma atomic emission spectrometry. Gravimetry was used to measure SiO₂ and SO₄ concentrations. Phenanthroline spectrophotometry was used to measure the Fe(III) concentration, and Fe(II) concentration was calculated by subtracting the Fe(III) concentration from the total Fe concentration. HCO₃ and Cl⁻ concentrations were measured using titration method. Two different electrodes were used to measure pH and electrical conductivity (EC). Geothermal water was flown at a rate of 1050 mL/min over the fiber sensor fixed in a bucket with tension applied to both ends. In inhibitor evaluation, the inhibitor solution was mixed with geothermal water by flowing it through a T-tube connected with the tube flowing geothermal water using a pump. The inhibitor concentration was calculated from the flow rate of the inhibitor solution and geothermal water.

Measurement of scale thickness. For measuring the thickness of scale formed on the quartz fiber core in geothermal water, quartz plates with dimensions of 10 mm × 10 mm × 2 mm were prepared. A small gold leaf was adhered to a part of the quartz plates. The plates were immersed into the bucket through which geothermal water flowed at 1050 mL/min. After a certain time, the quartz plate was taken out from the water. After removing the gold leaf from the quartz plates using an ultrasonic bath, the difference in thickness between the surface of scale formed and the bare surface of the quartz plates was measured by vertical scanning interferometry (MM5500; Ryoka Systems, Japan).

Table 3. Chemical composition of groundwater sampled in Sumikawa Geothermal Power Plant, Japan.

| Component | Value |
|-----------|-------|
| Temperature (°C) | 93.3 |
| pH | 6.48 |
| EC (mS/m) | 414 |
| Na (mg/L) | 680 |
| K (mg/L) | 110 |
| Ca (mg/L) | 16.0 |
| Mg (mg/L) | 0.05 |
| Cl⁻ (mg/L) | 1100 |
| SO₄ (mg/L) | 99 |
| SiO₂ (mg/L) | 980 |
| HCO₃ (mg/L) | 15 |
| Fe(II) (mg/L) | < 0.1 |
| Fe(III) (mg/L) | 0.04 |
| Al (mg/L) | 1.0 |

Laboratory study. The optical fiber was placed on a watch glass by applying tension to both ends of the fiber with the middle portion immersed in the solution at some distance from the bottom of the watch glass. The silica scale solution was prepared by dissolving sodium metasilicate (1000 mg/L) as SiO₂ in water at 90 °C. After the solution was neutralized to pH 8 by adding sulfuric acid, the exposed core of the fiber fixed on the watch glass was immediately immersed in the solution.

Field study. A field study was carried out in a geothermal water environment at Sumikawa Geothermal Power Plant, Japan (50,000 kW). Two-phase flow from SC-4 production wells is flowed into a 50 L simplified separator immediately immersed in the inhibitor solution and geothermal water.
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Author Contributions
T.O. wrote the manuscript and performed the experiments. T.O., A.U., A.O. supported in the experiments and preparation of the manuscript. H.K. who is acting as the corresponding author supervised the overall research work and in the manuscript evaluation.

Additional Information
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