INTRODUCTION

Over the years, glazes used in ceramics have been studied extensively. However, there have been few studies on the water stains that form on glaze surfaces. One of the most frequently encountered problems associated with the industrial use of silica is the formation of water scales in heat exchangers employed for geothermal power generation. In addition, the formation of water scales in bathtubs, sinks, faucets, and other sanitary ware is also a significant problem in daily life. Various approaches have been proposed for scale removal. For example, in Japan, "Osouji Rakuraku kagami" (easy-cleaning mirrors) coated with carbon to prevent the formation of water scales have been developed by TOTO Ltd. There are various studies on silica scale in geothermal plants, but the issue of silica scale in sanitary ware has not been well studied in the past.

It is known that scales formed on sanitary ware adhere to porcelain surface, adversely affecting the appearance of the sanitary ware and resulting in the formation of molds. The silica present naturally in water is the source of scales. It is considered that silica aggregates during the drying process and adheres to the surface of a ceramic ware to form a bulk scale. Factors such as temperature and humidity during the drying process affect water scale formation after drying. However, the influence of these factors on the surface adhesion of silica scale has not yet been elucidated. In addition, with respect to the adherence of the scale to sanitary ware, the removability of the scale has not been quantitatively

Abstract

The formation of silica scales from water on ceramics is a significant problem, and there is an urgent need to develop methods to prevent its formation or to remove it. In this study, we fabricated silica scales on glass substrates and investigated the effects of temperature and humidity during the drying process on the adhesion of the scales to the substrates. The scales were created from artificial water via a previously reported method, while focusing on the variations in the contact angle of water droplets on the substrates with changes in drying conditions. It was observed that the primary factors affecting the drying process are temperature and humidity. In addition, the drying rate of the droplets was in good agreement with the theoretically predicted value. Further, the scales were subjected to quantitative rubbing tests, and the scale removal rate was observed to be higher under humid conditions. The results obtained herein should aid efforts to develop methods for the easy removal of silica scales from substrates.

KEYWORDS

colloids, silica, silicates
evaluated. This study aims to investigate the effects of temperature and humidity during scale formation on the scale removability. Finally, we quantitatively discuss scale removal and the environmental factors that may affect it.

2 | EXPERIMENTAL PROCEDURE

2.1 | Sample preparation

Generally, commercially available water and tap water have different silica concentrations, which differ in each geographical region. Moreover, the amount of elements contained in it is not constant. Therefore, the concentration of silica is not constant because it is naturally derived. Therefore, artificial water was used in this study.

First, 22.08 mass% silicic acid anhydride (SiO$_2$) and 77.92% sodium carbonate (Na$_2$CO$_3$) were added to a platinum dish, melted at 1200°C in air, held at that temperature for 15 min, and allowed to cool rapidly. The obtained product was crushed to form a powder. Subsequently, this powder was mixed with ultrapure water to produce artificial water, and thereafter, a water scale was formed. In this study, artificial water samples with four different concentrations of silica (10, 100, 500, and 1000 ppm) were prepared. Figure 1 shows the procedure for producing scale artificial water on a glass substrate.

A 50 μL droplet of the prepared artificial water sample was placed on the glass substrate from a height of 2 mm. The substrate was then placed in a constant temperature/humidity chamber, and the water droplet was dried to form a scale. The temperature and humidity were varied within three levels, which were 25, 40, and 55°C and 50%, 70%, and 90%, respectively.

2.2 | Evaluation of contact angle of the artificial water scale on the glass substrate

The droplet of the artificial water sample was placed onto the substrate, which was then placed horizontally in a constant temperature/humidity chamber, and the state of the droplet was photographed from the side of the substrate. As shown in Figure 2, the contact angle of the droplet was determined from the photographs using the angle tool of the image processing software ImageJ. The left and right contact angles were measured three times, and the average value was taken as the contact angle.

2.3 | Sliding test

To quantify the removal rate of the formed scale, a sliding test was performed on the prepared scale using a rotary polishing machine, as shown in Figure 3. The rotation speed, pressure, and water flow rate were 10 rpm, 7.65 kPa, and 11.5 mL/s, respectively. The test was performed for 0, 15, 30, 45, and 60 min for each sample.

2.4 | Evaluation of appearance and crystalline morphology of the scale after sliding

After the sliding test, the scale sample was evaluated via laser microscopy (VK-9700, KEYENCE). The scale was evaluated by focusing on its circumference. The height, width, and cross-sectional area of the ring portion of the adhering scale were measured by irradiating the sample after subjecting it to the sliding test and detecting the intensity of the reflected laser beam.

Figure 4 shows the scale sample and height data obtained from the laser microscopy measurements. The length along the x-axis of the part shown in red in the figure is the width. The average value in the y-axis direction was taken as the height.

At the same time, the area depicted in red in Figure 4 was considered the cross-sectional area of the ring. The measurements were performed at five points per sample, and the average values were taken as the height and width of the sample. Then, volume of the remaining water scale was calculated by integrating the volume of the ring portion of the scale from

![Figure 1: Experiment of artificially created water scales](image_url)
\[ m(t) = -\pi R D'(1 - H) C_v (0.27 \theta^2 + 1.30) \]  

where \( R \) is the radius of the bottom of the droplet, \( D' \) is the apparent diffusion coefficient of water vapor in air, \( H \) is the humidity, \( C_v \) is the saturated water vapor concentration, and \( \theta \) is the contact angle. The constant temperature/
humidity chamber used in this study resulted in forced convection, and the effect of the airflow on the drying of the droplets was considered. Therefore, the apparent diffusion based on the mass transfer coefficient, \(k(\text{m/s})\), was considered, and the apparent diffusion coefficient, \(D'(\text{m}^2/\text{s})\), was calculated. The mass transfer coefficient is expressed by the following equation:

\[
k = \frac{ShD}{d},
\]

(2)

where \(Sh(\text{–})\) is the Sherwood number, and \(d(\text{m})\) is the diameter of the bottom of the droplet. Under conditions of turbulent flow along a flat plate, the Sherwood number can be expressed in terms of the Reynolds number \(Re(\text{–})\) and Schmidt number \(Sc(\text{–})\) as shown in the following equation:

\[
Sh = 0.037Re^{0.5}Sc^{-1/3}.
\]

(3)

The Reynolds number and Schmidt number were calculated using the following equations:

\[
\delta = \frac{D'}{k}.
\]

(4)

Figure 8 shows a comparison of the theoretically predicted and experimentally determined mass decrease value. The calculated values—are represented by solid lines, while the experimental values—are represented by symbols. From these results, it can be inferred that the evaporation rate at a given time could be correctly determined using Equation 1. The contact angle data indicate that higher temperatures and lower humidity values resulted in higher evaporation rates. Based on the calculated evaporation rate values, it can be concluded that the higher the temperature or lower the humidity, the higher the evaporation rate. Thus, as shown in Figure 9, the evaporation rate was the highest under high-temperature, low-humidity conditions.

We also focused on other factors affecting evaporation, such as those calculated using the above-stated equations as well as the thickness of the diffusion layer and diffusion
coefficient. Figure 10 shows the changes in the diffusion coefficient with temperature and humidity. The diffusion coefficient of a typical gas molecule generally increases proportionally with temperature, as given by the Stokes–Einstein equation (Equation 7).

\[ D = \frac{kT}{6\pi \mu \alpha} \]  

(7)

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \mu \) is the viscosity, and \( \alpha \) is the molecular radius.

Further, we attempted to investigate the decrease in apparent diffusion coefficient, \( D' \), in proportion to the temperature. \( D' \) was determined by fitting Equation 1 to the measured evaporation rate data. Considering the data for the water sample with a silica concentration of 1000 ppm at a humidity of 50% as an example (see Figures 3–6), the evaporation rate doubled as the temperature was increased from 25°C to 55°C. On the other hand, the saturated water vapor concentration changed from 23.019 to 103.929 \([\text{g/m}^3]\), which is approximately four times higher. In other words, since the increase in the saturated water vapor concentration on Equation 1 is more pronounced than the increase in the evaporation rate, \( m(t) \), as a result, \( D' \) decreases. This is because \( D' \) is an apparent value and a fitting parameter. It can also be seen that the thickness of the diffusion layer, \( \delta \), exhibits a similar trend as that of \( D' \).

Strictly speaking, the diffusion coefficient related to the reaction kinetics was not a meaningful parameter in this study. Generally, a diffusion layer forms around a water droplet, and the evaporation of water molecules into the atmosphere occurs through this layer. However, in the experimental system used in this study, there was an airflow of 2 m/s, which resulted in turbulence in terms of the Reynolds number. Therefore, even if a diffusion layer were to form, it would be quickly stripped by the surrounding airflow, and the reaction kinetics would no longer be valid.

According to a study by Erbil et al,\(^{16}\) the diffusion coefficient, \( D \), for water droplets (RH of 48%) at 0.249 (cm/s) is 24.9 (mm²/s). Although the order of \( D \) is correct, it can be seen that the diffusion coefficient value obtained in this study is extremely high. This difference can be attributed to the fact that Erbil et al used hanging-type droplets instead of dripping ones. In addition, they used a chamber for evaporation. Thus, the diffusion coefficient is also much larger than that for the static state; the static state is different from the evaporation state for a diffusion layer. Finally, the difference in the temperature dependence of the diffusion coefficient can be attributed to the occurrence of turbulence. However, further research is required on this topic.
3.2 Sliding test and removal rate

Figure 11 depicts the changes in volume, $V$, as calculated using Equation 8.

\[ V = \int_{0}^{2\pi} A d\theta \]  \hspace{1cm} (8)

where $A$ is the cross-sectional area of the ring portion of the scale and $\theta$ is the contact angle between the droplet and the substrate. $V$ of the circumferential part was obtained by integrating the cross-sectional area of the ring portion for the range of $\theta = 0$ to $\theta = 2\pi$. From the sliding test, it was confirmed that, in the case of all the samples, although there was a difference in the initial scale volume based on the concentration of the water sample used, the scale volume decreased with the sliding time. In addition, it was confirmed that, for the 1000 ppm sample, the scale remained on the substrate even after sliding for 60 min.

Further, assuming that the initial volume of the scale is $V_0$ and that the volume of the scale after being subjected to the sliding test for 60 min is $V$, the scale rejection rate, $R$, can be determined as follows:

\[ R = 1 - \frac{V}{V_0} \]  \hspace{1cm} (9)

Figure 12 depicts the relationship between the temperature, humidity, evaporation rate, and scale removal rate. The data in Figures 12, 13 imply that, during this study, the evaporation rate was higher under high-temperature and low-humidity conditions. As depicted in the graph in Figure 12, only the 90 wt% samples appear to have a lower removal rate. However, we believe that this is a tentative result, and we need to consider the phenomenon of glass-to-glass adhesion to explain these observations.

The mechanism of silica-silica adhesion remains a matter of debate. Moutinho et al.\textsuperscript{17} used atomic force microscopy to evaluate the adhesive force between a glass substrate and silica particles. They found that the higher the relative humidity, the higher the adhesive force. They cited the differences in the adhesion mechanisms as the reason for the increase in the adhesive force at higher humidity levels, stating that van der Waals forces dominate adhesion between glasses under low-humidity conditions while capillary attraction is the dominant force under high-humidity conditions. However, the results of the present study contradict those reported by them.

On the other hand, according to Lai et al.\textsuperscript{18} it is not the relative humidity itself but factors such as the formation of a thin film of water and the chemical properties of the surfaces involved that determine the adhesive strength of the silica scale. They demonstrated that siloxane bonds (Si–O–Si) are formed by the condensation of silanol groups at low relative humidity levels and that these bonds result in an unusually high adhesive strength. In this study, the removal rates for the 50 and 70 wt% samples were lower on average than that of the 90 wt% sample (i.e., the adhesive strength of silica was higher in the former cases). Note that in the case of the 50 and 70 wt% samples, the samples with the higher evaporation rates (i.e., the samples tested at higher temperatures) showed higher adhesive strengths for the same humidity level. Although the mechanism responsible for these results...
is elusive, it can be hypothesized that the adhesive strength is very high under temperature conditions because of the formation of siloxane bonds.

Looking at the macroscopic state of the water sample as well as the silica–silica bond, the porosity of silica becomes very high under certain conditions, as described in. It is possible that the porosity was increased by controlling the temperature and humidity in this experiment as well. As mentioned above, it is certain that siloxane bonds also affect the adhesion of water scale. However, in the present results, the longer evaporation time of the water sample can be considered to have resulted in a coarser macroscopic state of the water sample.

To confirm this hypothesis, it is necessary to examine the scale–substrate interface using cross-sectional transmission electron microscopy or to examine the structure of the scale itself using scanning electron microscopy. In any case, further investigations are required at this stage.

4 | CONCLUSIONS

In this study, we generated a silica scale from artificial water samples under different drying conditions by varying temperature and humidity. We theoretically modeled each drying process and confirmed that evaporation is dependent on the evaporation rate. The apparent diffusion coefficient, \( D' \), for evaporation was derived by fitting the obtained data to the evaporation rate equation. It was confirmed that \( D' \) does not have the usual temperature dependence and, in this case, does not increase proportionally with temperature because an increase in the saturated water vapor concentration had a significant effect. Sliding tests were performed on the different scale samples. It was confirmed that most of the scale samples could be removed within 15 min under the experimental conditions in this study. The removal rate was higher under high-humidity conditions. We hypothesize that this is because of the self-adhesion of silica and the bonding state of the scale surface. However, additional research is necessary to confirm this hypothesis.

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