Coffee-ring-effect-induced water scale formation of silicic acid-containing droplet

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Abstract
The drying behavior of silicic acid-containing water droplets on a glass substrate was investigated by using as-prepared aqueous silica solutions of varying concentrations to simulate water scale-like formation. The droplets of aqueous silica solution were found to form circumferential solid silica deposits (water scale). Additionally, the drying behavior of the silica droplets was observed under varying temperature and humidity. Optical microscopy images of the deposited material showed thicker deposits in the inner part of the circumference, indicating the so-called rush-hour effect and induced by the coffee-ring effect. Thus, the formation of water scale observed in daily life can be attributed to the coffee-ring effect. Scanning electron microscopy confirmed that the as-prepared water scale consisted of polymerized silica spheres. The hardness of the water scale depended on the amount of silica deposited and the initial concentration of the silica solution. Thus, the formation of water scale in daily life was concluded to occur by two mechanisms: formation of silica spheres by silica polymerization and agglomeration-deposition by the coffee-ring effect.

Keywords
silicates, evaporation, indentation

1 | INTRODUCTION

The formation of water scale is inevitable, particularly at sites of water circulation such as kitchens and bathrooms. Water scale formation is observed on surfaces that are in contact with water, such as bathroom mirrors, water taps, washstands, and toilets. Water scale formation is due to the presence of silica, which is commonly found in normal drinking water and foods.1 A silica-containing water droplet adheres to the solid surface and evaporates to reduce its volume, thereby aggregating the silica in the droplet. Consequently, polymerized silicic acid becomes chemically bonded to the solid surface.

Recently, water scale removal and prevention have gained considerable research and industrial attention. In the geothermal field, the removal of water scale adhered to heat exchangers has been challenging; McCartney et al state that “The formation of scale is a serious problem in industrial heat transfer” in Ref.2 In general, silica strongly adheres to solid surfaces. It can be removed by rubbing or prevented by the addition of polymers before adhesion. It is presumed that silica-containing water droplets dry by evaporation and the residues of the droplets aggregate (the coffee-ring effect) to form water scale.

Deegan et al3 analyzed the mechanism of the coffee-ring effect and confirmed the occurrence of pinning at the
circumference. However, the mechanism of the coffee-ring effect in water scale formation has not yet been clearly elucidated. Thus, for this study, we assumed that silica particles in tap water experienced polymerization and were deposited in ring shapes because of the coffee-ring effect. As is commonly known, the coffee-ring circumferential part of a deposit is strongly adhered to the substrate. Elucidation of this adhesion mechanism may resolve the water scale formation problem occurring on daily-use fixtures such as toilets, sinks, and showerheads. Although the occurrence of the coffee-ring effect in droplets of other liquids has been investigated, the coffee-ring effect in a silica substrate that causes water scale formation has not yet been reported.

In this study, the drying behavior of silicic acid-containing water, which is the condition underlying water scale formation, is discussed. By studying the drying behavior of silica-containing water droplets on a glass surface, the mechanism of water scale formation on silica-based ceramics is elucidated.

## 2 EXPERIMENTAL PROCEDURE

Commercially available tap water has different silica concentrations depending on its area of production. In addition, the silica concentration of mineral water is not guaranteed because it contains naturally occurring silica. Thus, in order to evaluate water scale formation, a uniform aqueous silica solution is prepared.

For the silica-containing solution preparation, the following requirements were satisfied:

- Silica-containing water must comprise quantitative and general-purpose substances
- Silica-containing water should have a simple system (no Ca, Mg, or other elements).
- Silica-containing water must be able to form water scale

First, 1.0 g of anhydrous silicic acid (SiO₂) and 4.0 g of sodium carbonate (Na₂CO₃) were melted at high temperature (1200°C) in a Pt dish. The molten liquid was diluted in distilled water to prepare 1 L of the as-prepared silica-containing water. Silica is present as a monomer in this solution. The silica concentrations in the as-prepared silica-containing aqueous solutions were 1, 10, 100, and 1000 ppm. In the experiments, 10 μL of the solution with each silica concentration was deposited as droplets on an amorphous SiO₂ glass substrate and dried under various constant temperatures and relative humidity (RH) values, as shown in Table 1.

After drying, the state of the circumferential part of the 100-ppm silica-containing deposit before and after rinsing in distilled water was observed with an optical microscope (OM). Then, using the sample with the highest concentration of 1000 ppm, the height distribution of the ring was measured using a laser microscope (VK-9700, KEYENCE). The result in Figure 2 confirms whether the coffee-ring-like deposit is formed with the prepared solution. In addition, using the 1000-ppm sample, the change of the liquid droplet with drying conditions was observed with an optical microscope. Table 1 summarizes the experimental drying conditions. All dried samples were prepared at 1000 ppm and standard conditions at 23°C and 50% RH. According to the conditions of humidity and temperature were changed. The dried droplet was rinsed with distilled water and blown with dry air. This process removed the upper layer of silica that was not adhered to the substrate. After the drying process, deposits in the circumferential part were observed.

Silica crystals formed by precipitation at some parts of the deposits were also observed. The bottoms of the deposits were strongly adhered to the substrates, while the upper layers were not adhered but simply rested on top as crystals. The samples evaporated under various conditions were observed by OM and scanning electron microscopy (SEM; Hitachi High-Technologies model S-4800). The measurement conditions were room temperature (23°C) and 50% RH. A 2-nm Os coating was added to the samples as pretreatment for SEM. At the time of SEM measurement, the sample was fixed to the measurement base with an adhesive. The hardness of the circumferential part was measured at various silica concentrations (1, 10, 100 ppm) by a nanoindenter (ENT-2100, Elionix) at room temperature 23°C and 50% RH. The indentation weights were all fixed at 0.2 mN. Ten points of indentation were measured to calculate one point as the average hardness.

## 3 RESULTS AND DISCUSSION

Figure 1 presents the OM results. Figure 1A shows the sample of 100 ppm that was evaporated at 25°C and RH 50%. Figure 1B shows the sample of 100 ppm after rinsing with distilled water to remove the upper layer. As shown in Figure 1B, interference fringes are observed at the circumferential part after washing the sample. This edge part of the coffee ring is adhered firmly to the substrate. Hence, this part remains after washing with distilled water and forms water
scale. The red circle in Figure 1B indicates the nanoindenter measurement points described later.

Figure 2 indicates the height distributions of the dried silica ring for the 1000-ppm sample, as measured by OM before washing. It shows that typical coffee-ring deposition has occurred along the circumferential part. The peak height of the circumference is approximately 500 μm. Most of the adhered silica is aggregated in the circumferential part, and the crystalline silica in the inner part is lower in height than the circumferential part. This phenomenon in which most of the silica is deposited on the circumferential part is based on the pinning effect.3 In order to cause the circumferential deposition of silica, outward flow under constant contact radius (CCR) conditions and colloidal deposits are required. According to Figure 2, most of the silica in the as-prepared silica-containing solution is deposited on the circumference of the ring with a diameter of approximately 5000 μm.

Photographs of the entire droplet and the circumference are obtained for each condition and shown in Figure 3. Under each condition, crystal growth is observed both at the circumference and inside the ring. At 75°C and 50% RH, which seems to cause the fastest drying, crystals with large grain sizes are observed. Under slower drying rates, dendritic crystal growth is observed in some areas, as shown in Figure 3A,B,D. In addition, island-like growth is observed with the slowest drying process (Figure 3C).

The photographs of the rings taken with a laser microscope for the samples of 1, 10, and 100 ppm are shown in Figure 4. Each scale formation differs, and the maximum
The height of each sample is shown in Table 2. The circumference of the ring is about 20 μm in (a) and (b), and 20-30 μm for the highest silica concentration (c). Thus, the concentration affects the height, but not the width, of the coffee ring. That is, the coffee ring is a single-ring structure. However, for the 100-ppm sample in Figure 4C, a second ring structure is also observed. As shown in Figure 4A,B, the peak heights are on the inner parts of the rings. The ring shape is nonuniform for the 100-ppm sample. At all concentrations, a crystal structure is observed inside the ring. In Figure 4A,B, bulk crystals are observed to have precipitated inside the ring, but dendritic crystals are precipitated in the 100-ppm sample in Figure 4C.

Figure 5 shows the measurement results of the nanoindentor. As shown, higher silica concentrations correspond to greater hardness variations, but also to higher hardness values. The hardness of the quartz substrate is 8398 N/m², confirming that the deposits are softer than the substrate.

Figure 6 shows 50 000× magnified images of the ring circumferences for different silica concentrations. Figure 6A,B show that colloidal silica is aggregated to form a ring. They also indicate that differences in silica concentration yield differences in the colloidal silica density. The mechanism of adhesion between the water scale and substrate cannot be determined from this figure; however, according to McCartney et al., silicic acid in an aqueous solution polymerizes to form spheres in porous-like structure. The SEM images show that the 1-ppm sample is lower in polymer sphere density than the 100-ppm sample. The SEM images in Figure 6 confirm that silica forms a particle structure by polymerization and that the polymerized silica spheres become aggregated to form bulk scale. The shift in the crystal structure growth from dendritic to island-like is also observed with increasing humidity.

As described above, the ring-shaped particle deposition is attributed to the coffee-ring effect. In this observation of the coffee ring, it was found that the inner part of the ring showed a large height. The mechanism of ring formation is generally attributed to the rush-hour effect, in which circumferential outward flow accelerates rapidly at the last stage of drying. Figure 2 confirms that the water droplets are deposited circumferentially by drying on a glass substrate at room temperature.

An important premise of material deposition by the coffee-ring effect of a suspension is the evaporation form. Picknett et al. have proposed the CCR form of evaporation, in which pinning occurs at the edge of the water droplet and the end part remains fixed while evaporating. As described by Deegan et al., the outward flow in the droplet in the coffee-ring effect arises from capillary flow. Eral et al. also note that coffee-ring hysteresis is important, as is the case with evaporation-induced capillary flow. As described by Ooi et al. and Marin et al., the first half of coffee-ring formation occurs by very slow outer flow deposition, but the final stage occurs by the rush-hour effect. According to Marin et al., most of the deposition in the coffee-ring effect occurs in the last part. The rush-hour effect is caused by generation of a volume flow in the circumferential portion by evaporation at the droplet surface. In this experiment, silica particles were precipitated as the solution evaporated. According to the result from Figure 2, because most of the silica particles are deposited at the circumference, a rush-hour effect may occur at the end of the droplet evaporation process in which most of the silica particles are deposited along the circumference.

Shahidzadeh et al. compared the method of producing coffee rings in a general suspension system such as CaSO₄,
which has low solubility, and a completely soluble system, such as NaCl. Their results confirmed that coffee rings were formed in the CaSO₄ system, although the rings differed depending on the substrate cleaning conditions. However, in the NaCl system, no coffee ring was formed; instead, NaCl crystallized in the central part of the droplet. They concluded that no circumferential deposition occurred in the NaCl system because of crystal formation at the liquid-air interface of the droplet. In our experiment, the experiment confirmed that silica particles were deposited on the circumference. Comparing our experimental results with that of NaCl, the crystal size is important. Shahidzadeh states in Ref.10 that “For NaCl, reproducibly only one or a few crystals form, and with such a small number it is difficult to form a coffee stain, even if they would remain near the contact line.” In other words, although silica is precipitated in our experimental system, it behaves like a general colloid suspension because of its particle-like shape, rather than as a single large crystal, thus forming the coffee ring.

**TABLE 2** Difference of height at various silica concentration

| Silica Concentration | Height of ring peak (μm) |
|----------------------|--------------------------|
| 1 ppm                | 1.9                      |
| 10 ppm               | 2.9                      |
| 100 ppm              | 6.1                      |

Our experimental results agree with those observed in real systems of water scale formation. In addition, the results of the naindenter test showed that the hardness of the circumferential part was increased with increasing concentrations of silica in the aqueous solution. To support this result, it must be first noted that the silica particles produced by polymerization are bonded together. In the past, research has been conducted on simulations regarding the bonding of particles after silica polymerization.

Becit et al.¹¹ showed that the formation of water-derived oligomers between two silica particles results in the binding of the two silica particles. The results shown in Figure 6 also indicate that the silica spheres aggregate to form a single structure, which may be attributed to the process proposed by Becit et al. Further, the density of bonds is determined by the initial concentration of silica. Because of these factors, the polymerized silica particles combine to form a bulk silica scale. The coarseness and density of the particles determine the strength of this silica scale. According to Kanaoka et al.,¹² the shear strength is affected by material density. Luo et al.¹³ report that the Vickers hardness decreases with increasing porosity. Both Kanaoka and Luo suggest that the density of the porous material affects its strength. Therefore, also as confirmed in this experiment, the indentation hardness is reduced because of the enhanced porosity. This experiment revealed the basic mechanism of water scale formation. The droplet of mineral-bearing water polymerizes during the drying process to form particles. The particles gradually approach the circumference by the coffee-ring effect as they dry. As the particles dry, they are sequentially bonded to form a bulk in which spherical particles are connected.

**4 | CONCLUDING REMARK**

We succeeded in forming artificial water scale by dropping as-prepared silica-containing water onto glass. The results confirmed that the artificial water scale was deposited in a coffee-ring-like structure.

We confirmed that the internal crystal state differed depending on the drying conditions. In addition, artificial water...
scale was produced from the agglomeration of silica particles. This particle agglomeration produced a bulk silica scale.

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