The Formation of Insoluble Stains on Glass and Glaze Surfaces

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The formation of insoluble stains on glass and glaze surfaces was studied in laboratory scale. The samples were dipped in acidic, alkaline and aqueous solutions and the analysis of the surfaces were carried out by SEM and AFM. The defect formation was found to be initiated by the impurities in tap water being left on the surface after water was dried off. All other residual chemicals could be cleaned away except silica which remained insoluble on the surface. The silica orginated from the tap water and was not a result of a corrosion of the surface.

1. Introduction

During the past years, defects in the form of hard, drop-like stains on the surface of sanitaryware glazes and shower glasses have been reported. In some cases the stains are noticed already after a few weeks' exposure to aqueous media, but for some cases these kinds of stains are reported only after several years. These stains could not be entirely washed away by commercial cleaning agents. It's well known that stains are formed on surfaces for example in bathrooms when using hard water. These lime containing stains can usually be removed by using an acidic washing. It's also known that glaze or glass surfaces can be affected by acidic, alkaline or water solutions[1,2]. By corrosion of glasses or glazes, alkali ions are usually extracted into the solution in preference to silica and the other constituents of the glassy matrix. An alkali-deficient leached layer is formed on the surface. The thickness of these silica-rich films, and probably their compactness, vary with the composition of the glass, the exposure time and temperature as well as the pH. The quality of tap water has also changed during the past decades. More and new chemicals are used for cleaning the water and the iron and calcium contents have for a long time caused problems with staining of surfaces.

2. Experimental Procedure

The formation of the stains was examined by dipping samples in different types of solutions. The samples were automatically dipped in each solution at the interval of 1 hour. The samples were held in the solution for 10 seconds, and between the dippings they were allowed to dry in normal room conditions. The samples were analyzed after dippings of 100, 250, 500 and 1000 times.

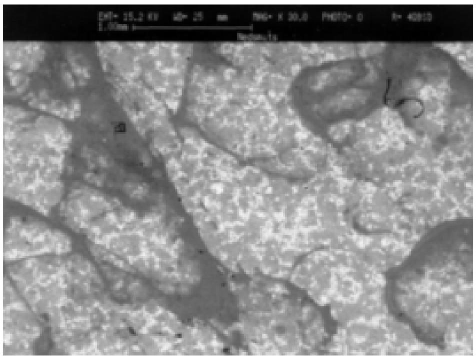
The samples were dipped in the following media; 10 % NaOH, 0.1 M HCl, saturated $CaCO_3$ solution, 1.5 g/l $Ca(OH)_2$ solution, distilled water, 4 different tap waters, natural well water, ion exchanged water and modified water.

The stain formation was studied on ceramic glazes of various compositions. Similar tests were carried out with reference surfaces of glass, aluminium and stainless steel surfaces.

All surfaces were analyzed by scanning electron microscope (SEM) equipped with energy dispersive X-ray analysis (EDXA). Some of the surfaces were further analyzed by atomic force microscope (AFM). The amount of Si in tap water was analyzed by inductively coupled plasma (ICP).

3. Results and Discussion

Analysis of the returned claimed glaze surfaces were first performed. The surfaces were cleaned and the insoluble parts were analyzed by SEM. The hard, drop-like stains on the surfaces were visible already by naked eye (Figure 1). Further analysis by EDX showed that the stains mainly consisted of Si. An analysis of the thick layer on uncleaned samples showed besides Si also Ca, Cu, S, and Cl (Figure 2). These impurities originated both from the daily usage of the bowl and the water used. The same result was found for several different samples.



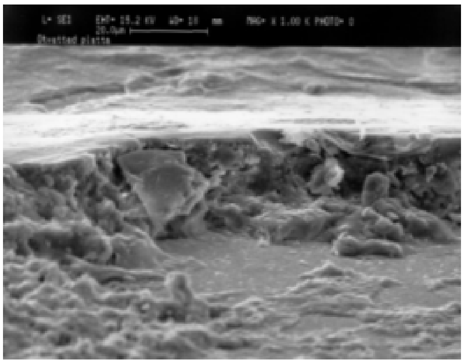
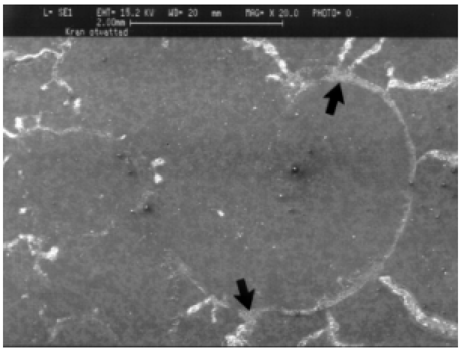


Figure 1. SEM micrograph of cleaned returned glaze surface showing stains (dark areas).

Figure 2. SEM micrograph of the thick coating on an uncleaned surface.

The formation of the stains was first studied by dipping glazed tiles in different types of solutions, i.e., NaOH, HCl, $CaCO_3$, $Ca(OH)_2$, distilled water and tap water. When exposed to tap water in laboratory tests the experimental glazes showed a similar deposit of a silica gel on the surface as reported for sanitaryware glazes in use. Glazes dipped in NaOH showed also a deposit formation. This deposit containing mainly sodium salts was easily removed by washing the surface. Glazes dipped in the calcium solutions showed a deposit consisting of calcium salts. These coatings were, though, easily removed by acidic washing. However, glazes dipped in distilled or ion-exchanged water or HCl showed no deposits. These preliminary results led to a comprehensive study of the durability of the glaze surfaces as a function of the glaze composition as well as the content of minor components in different tap water systems. Also the influence of the firing parameters was included in this study.

In the test series all glazes showed a similar formation of an insoluble silica gel on the surface when exposed to several tap waters (Figures 3 and 4). The stain formation could be noticed already after 250 dippings. However, if the samples were cleaned immediately with a cloth after every dipping, no stain formation could be noticed. The topography of the surfaces was studied by AFM (Figures 5 and 6). The average thickness of the deposits was 0.620 μm but even thicknesses more than 1 μm could be found. The average roughness (0.045 μm) of untreated surfaces indicates that there are good opportunities for the particles to attach to the surface thus initiating the stain formation. All these results indicate that neither the glaze composition nor the firing schedule had a major influence the stain formation.



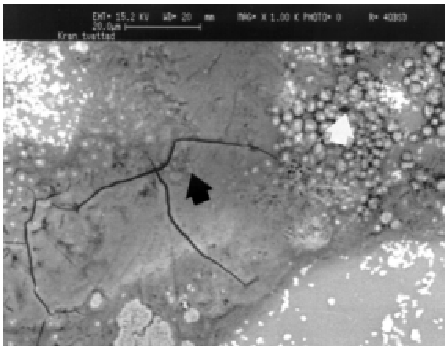
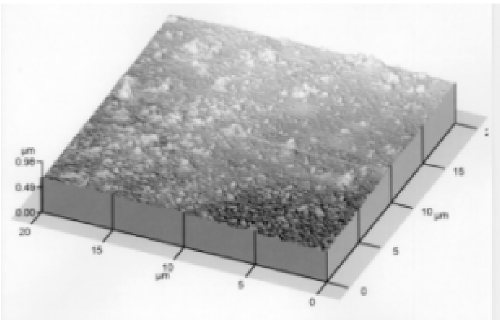


Figure 3. SEM micrograph showing stain formation on glaze surface.

Figure 4. SEM micrograph showing Si-rich (black arrow) and Ca-rich (white arrow) regions.



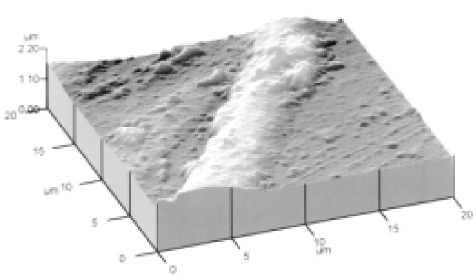
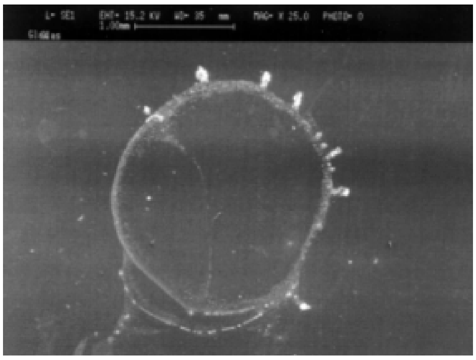


Figure 5. AFM image showing the topography of a normal untreated glaze surface.

Figure 6. AFM image showing the topography of a glaze surface showing stain formation.

Similar experiments with the reference materials aluminium, stainless steel, acid resistant floor tile and glass were performed. Similar deposits to those on glazed surfaces were found also on all glass surfaces dipped in tap water. After cleaning, an insoluble Si-rich stain remained on the surface. The stain was even easier to notice on a transparent glass sample than on the other materials. The SEM and AFM images confirmed that the deposits laid on the surface and had not penetrated through the surface (Figures 7 – 10). The formation of a silica gel on the surface could also be observed for the other reference materials dipped in the tap waters. Similar Si-rich stains could also be found on the stainless steel and aluminium samples containing no Si in the material itself (Figure 11 and 12). This indicates that the origin of the stains can be traced back to deposition of impurities in the tap water rather than on dissolution and resorption of corrosion products of glaze or glass components on the surfaces. Besides the silica gel rich stains, usually also stains containing calcium, sulphur and chloride could be found on the surfaces, but by careful acidic washing these components could be removed from the stains leaving only the insoluble silica gel on the surface.



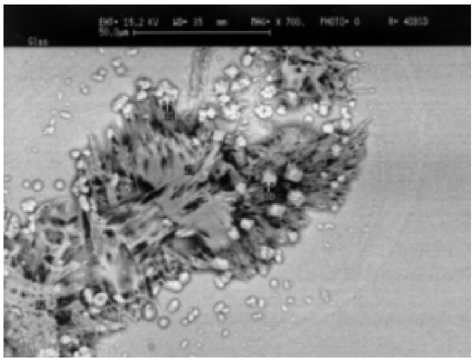
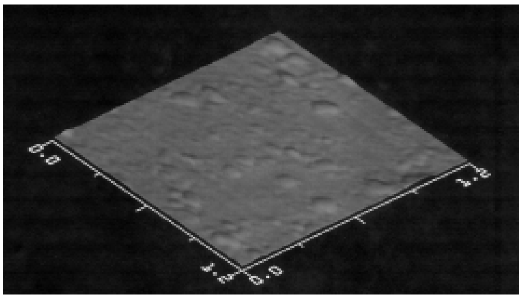


Figure 7. SEM micrograph showing stain formation on glass surface.

Figure 8. SEM micrograph of Si- and Ca-rich deposits on glass surface.



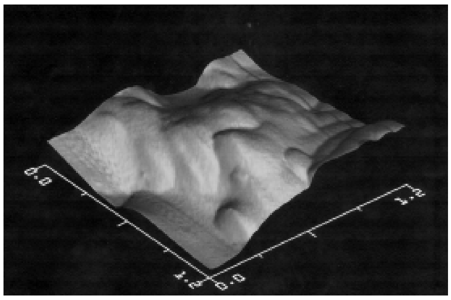
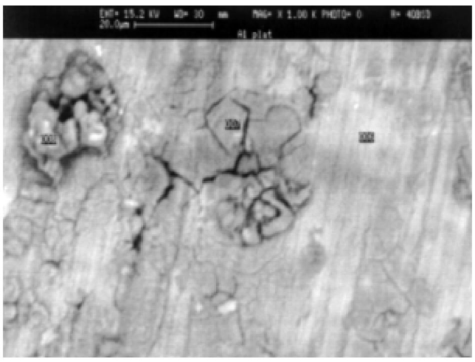


Figure 9. AFM image of untreated glass surface.

Figure 10. AFM image of stain formation on glass surface.



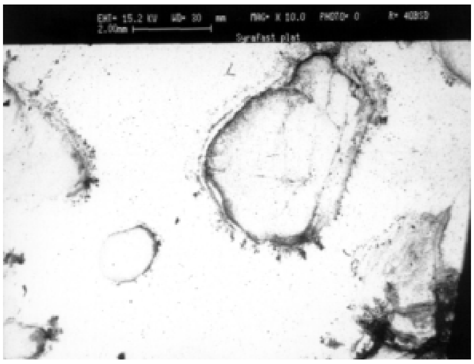
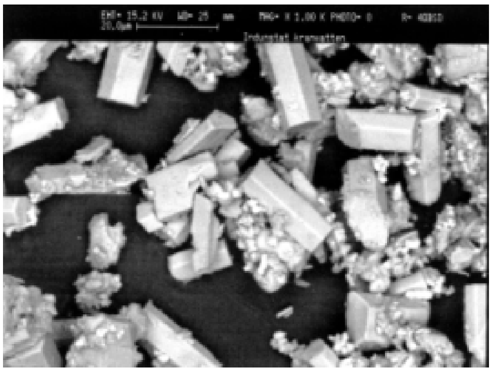


Figure 11. SEM micrograph of Si-rich deposits on aluminium substrate.

Figure 12. SEM micrograph of Si-rich deposits on stainless steel surface.

An EDX-analysis of several evaporated tap waters showed a significant amount of residual chemicals consisting mainly of Ca, Mg, Na, S, Cl and Si (Figures 13 and 14). The same elements were found also in the stains on the examined surfaces after water exposure thus indicating the origin of the stain formation. The average amount of Si in the residues of evaporated tap waters was about 10 % but waters with up to 30 % Si (calculated as oxide-%)

were found. ICP-analysis gave an average of 2.7 ppm Si in tap waters. The results showed that the more Si in water the more distinct was the insoluble deposit on the surface. A further confirmation of the origin of the stains was carried out by producing a simulated water containing the salts found in the tap water but by leaving out silica. When using this simulated water no formation of a silica gel on the surface could be observed.



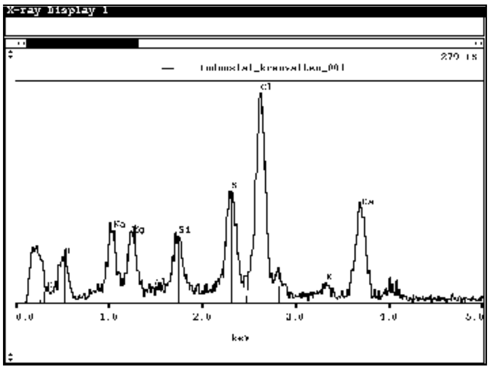


Figure 13. SEM micrograph showing products of evaporated tap water.

Figure 14. EDX analysis of the products in figure 12.

4. Conclusions

The stain formation on glazed surfaces was found to be initiated by impurities in the tap water being left on the surfaces after the water is dried off. If the preliminary stains are removed immediately, no damage of surface can be observed. However, if the surface is washed first after several weeks of exposure, silica will be strongly bound at the surface and a permanent damage will be formed. The formation of the stains depends on how well the water drop remains on the surface (surface tension), how often the surface is cleaned, the humidity, i.e., how fast the surface dries, the amount of Si in the water, and eventually the shape of the body surface. The changes in the composition of the salts dissolved in the tap water system are supposed to be the main reason for the observed “delayed” damages of the old glaze surfaces. These results indicate that the composition of the salts dissolved in tap waters nowadays are likely to give stains on glass and glaze surfaces thus putting new demands on the development of surfaces that can be easily cleaned.

Acknowledgements

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[1] R.G.Newton, Glass Technol. **26(1)**, p. 21-38 (1985)

[2] *Corrosion of Glass, Ceramics and Ceramic Superconductors*, edited by D.E. Clark and B.K. Zoitos (Noyes publ., 1992).