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Chemical resistance and cleanability of glazed surfaces

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Abstract

Adhesion of soil on glazed surfaces and their cleanability depends on chemical composition, phase composition, and roughness of the surface. The surface can be glossy consisting mainly of a smooth glassy phase. A matt and rough surface consists of a glassy phase and one or more crystalline phases. The origin and composition of the crystalline phases affect the chemical resistance and the cleanability of the surface. Fifteen experimental glossy and matt glazes were soaked in a slightly alkaline cleaning agent solution. The surfaces were spin-coated with sebum, i.e. a soil component typical for sanitary facilities. After wiping out the soil film in a controlled manner, the surface conditions and the soil left were evaluated with colour measurements, SEM/EDXA and COM. The results show that wollastonite-type crystals in the glaze surfaces were attacked in aqueous solutions containing typical cleaning agents. This corrosion led to significant decrease in the cleanability of the surface. The other crystal types observed, i.e. diopside and quartz crystals were not corroded, and the cleanability of glazes containing only these crystals was not changed in the cleaning agent exposures. Also the glassy phase was found to be attacked in some formulations leading to a somewhat decreased cleanability. The repeated soiling and cleaning procedures indicated that soil is accumulated on rough surfaces and surfaces which were clearly corroded by the cleaning agent.

Keywords: Scanning electron microscopy (SEM); Corrosion; Crystallization; Surface roughening; Polycrystalline surfaces; Crystalline–glass interfaces; Grain boundaries; Ceramics

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1. Introduction

Traditionally a glazed surface is regarded as an easy-to-clean surface. However, surface pitting and degradation in service diminishes its cleanability because of increased surface roughness. Surface degradation can also lead to opening of closed porosity in the glaze thus leading to micro-scale holes, which are often hard to clean by conventional cleaning techniques. Glazed surfaces have recently been coated with special functional layers to achieve soil-repelling surfaces. Mechanical properties and durability of new soil-repelling surfaces in service is still poorly understood. If the original glazed surface has a good chemical resistance in different environments, surface properties are likely to be further improved by special functional coatings. However, a surface failing in every-day environments gives a poor base for special coatings. Thus, basic knowledge of surface properties is essential for developing better glazes and functional coatings to be applied on glazes.

Chemical resistance in service, especially in corrosive liquid environments, is a major reason for applying glazes on ceramics [1,2]. When glazed tiles are used for floor covering, slip resistance of the surface should be considered. Slip resistance is usually attained by adding in the surface crystalline components or by adjusting the glaze composition is such a way that crystals are nucleated and grown in the surface during firing. Thus, a glaze might contain both a glassy phase and different crystalline phases for achieving desired properties. The amount of crystalline particles can be up to 20% in traditional mat glazes, while transparent and highly glossy glazes consist almost entirely of a homogeneous glassy phase. Differences in durability of crystals and glassy phase can lead to selective corrosion of the surface in certain environments. Chemical durability of glazes is usually discussed in terms of durability of the glassy phase in accordance with glasses. Glasses react in acidic environments by ion exchange of alkali ions by hydrogen ions. In alkaline environments the network structure of glass is destroyed by hydroxyl attack [1–5]. The influence of different oxides on durability of commercial glasses and glossy glazes is well understood. However, chemical resistance of glazes consisting of one or several crystalline phases embedded in a glassy matrix has not been widely studied. Wollastonite and anorthite crystals devitrified from a fritted glaze have been reported to be attacked by acidic solutions [6]. Wollastonite crystals in fast-fired raw glazes are attacked by acidic and also slightly alkaline water solutions [7,8].

Raw glazes are mixed of powdered water-insoluble minerals, while the main component in fritted formulations is a pre-melted glass. When using fritted formulations, the development of different phases in the glaze during firing is quite easily mastered. Raw glazes are because of their lower cost attractive for ceramics fired to above 1200 °C, i.e. floor tiles, sanitary ware and porcelain. The high firing temperature and several hours' firing cycle in traditional firing ensures that even the slowest reaction, dissolution of quartz, will be completed. The formation of crystalline phases in traditionally fired glazes takes place according to equilibrium reactions and is controlled by the total oxide composition of the glaze. However, in a modern fast-firing process of floor tiles the short firing cycle of 60–90 min restricts the extent of raw material reactions. Crystalline phases reported in fast-fired raw glazes are typical for primary reactions between the raw materials [9]. The surface is often unmature and its chemical and mechanical properties are poorly understood.

In this work chemical durability, soiling and cleaning properties of fast-fired raw glazes were studied with the focus on phase composition and topography of the surface. Altogether more than 30 different compositions have been tested for the development of surface phase composition and chemical resistance. Soiling of selected surfaces has been performed by model soils typical for sanitary facilities, i.e. environments where glazes surfaces are commonly used. Chemical resistance has been tested with model detergents containing components typical for household chemicals.

2. Experimental

Experimental glazes were ball-milled of commercial grade raw materials of kaolin, feldspar, dolomite, whiting, wollastonite, corundum and quartz. The compositions were however somewhat simplified by omitting the heavy metals and opacifying components often used in commercial glazes. The oxide compositions were chosen statistically within the compositional field of interest for glazes used in floor tiles as well as in sanitary ware ceramics, cf. Table 1. The method of choosing the experimental compositions does not take into account e.g. thermal expansion characteristics of the tile and glaze. Thus some problems with surface quality were supposed to arise. However, the approach allows estimating the effect of the glaze composition on the development of different crystalline phases during firing. The glaze suspensions were applied on green floor tiles in a waterfall coating process. The firing was performed in an industrial kiln with a top temperature 1215 °C and a total firing cycle of one hour.

Chemical resistance of the surfaces in a typical weakly alkaline cleaning agent solution was tested by soaking test pieces of the size 24 mm × 24 mm in 40 ml of a 4% detergent solution consisting of soap and a non-ionic surfactant (pH = 9.2) for two days after which the solution was changed to a fresh one and the immersion continued for two more days. After soaking the test pieces were washed in ultrasonic bath, once in distilled water and twice in ethanol. Phase composition of both non-treated and soaked glazes was analyzed with SEM/EDXA (LEO 1530, Vantage EDXA from Thermo Noram) and XRD (X'pert by Phillips). The gloss was measured with reflectometer (REFO3 by DRLANGE). Surface topography was measured by Confocal Optical Microscope, COM (μ Surf by NanoFocus). Average surface roughness R_a, was measured for 250 × 250 μm surfaces, and surface roughness profile was measured for 1460 μm lines along the surfaces.

Table 1
Limits of oxides in experimental glazes (wt%)

Oxide	Minimum (wt%)	Maximum (wt%)
Na_2O	1.8	4.6
K_2O	2.2	5.4
MgO	0	4.0
CaO	5.0	30.0
Al_2O_3	9.9	25.0
SiO_2	45.4	77.1

Both non-treated and soaked samples were soiled by spin-coating with 20 μl of a soil solution consisting of ethanol (50 ml), sebum (212 mg), and soot (50 mg) as a colour marker. In order to achieve a layer that easily could be measured by spectrophotometer (Lamda-2 UV–VIS with Labsphere RSA-PE-20 by Perkin Elmer) the soiling was repeated four times with 15 s drying between each soiling step. After 24 h the glazes were cleaned in a MiniCleanabilityTester with moist (100% water content) floor cloth. The cloth was pressed to the surface with a hydrostatic pressure of 0.5 bar and the cloth was rotated once on the surface. The cleaning degree was calculated from the Lab-colour coordinates measured for unsoiled, soiled and cleaned test pieces according to the formula [10]

$$\text{Cleaning degree}(\%) = (\text{DE}_{\text{cleaned}-\text{soiled}})/(\text{DE}_{\text{unsoiled}-\text{soiled}}) \times 100\%$$

where colour coordinates for each combination of surfaces is given by

$$\text{DE}_{1-2} = \left[(a_1 - a_2)^2 + (b_1 - b_2)^2 + (L_1 - L_2)^2\right]^{0.5}$$

After the first cleaning the pieces were soiled and cleaned three more times according to the procedure described above in order to study accumulation of soil on soil.

3. Results and discussion

Gloss value of the experimental glazes varies from 2% for the surface with a high amount of crystals to 82% for the surface with some crystals embedded in the glassy matrix. Average surface roughness, R_a, increases with increasing crystal content and decreasing gloss value. For the glossiest surfaces R_a is around 0.1 μm, and increases to around 0.5 μm for matt glazes with gloss value between 30% and 40%. At lower gloss values the average roughness rapidly increases to more than 4 μm. The crystalline phases in the surfaces were identified as diopside, wollastonite, pseudowollastonite, corundum and quartz by XRD and SEM/EDXA. The first three types are formed in the sintering reactions while the two latter ones are likely to be residual raw materials. Diopside and wollastonite crystalline are formed just below the top firing temperature and are typical for fast-fired glazes [9]. Surface properties of the experimental glazes are summarized in Table 2 by the different combinations of diopside, wollastonite and pseudowollastonite crystals in their surfaces. Glazes with high magnesia content contain mostly dolomite crystals, while wollastonite crystals are found in compositions with high lime content. Pseudowollastonite is formed only in compositions with very low magnesia content. All the glazes contain residual quartz and some glazes also corundum.

Cleaning degree of both untreated and in detergent solution soaked glasses are also given in Table 2. Cleaning degree is better than 80% for glazes with gloss higher than 30%. Cleaning degree in this work refers to only a short cleaning effort, and will be better for the glossy surfaces when continued. Cleaning degree is poor for the rough and very matt surfaces despite of the phase composition of the surface. However, after soaking the surfaces in the alkaline detergent solution, differences in cleaning degree were observed for surfaces containing different crystals, cf. Table 2. The differences could be explained by selective dissolution of wollastonite and pseudowollastonite crystals from the surface. Chemical durability of diopside crystals was found to be good. In Fig. 1 is shown SEM-images of two surfaces both before and after soaking.

Before soaking both columnar wollastonite and hexagonal pseudowollastonite crystals and darker quartz crystals were identified in Glaze 13 E. After soaking black holes in the surface left by dissolved wollastonite and pseudowollastonite crystals can be seen. Only wollastonite crystals were identified in Glaze 11 E. After soaking these crystals were partly dissolved and residual quartz crystals around which wollastonite was nucleated are revealed.

Repeated soiling and cleaning of the experimental surfaces showed that soil is accumulated on surfaces with the lowest gloss and highest roughness. Photorealistic COM-images of Glaze 11 E before and after soaking is given in Fig. 2a and b. The wollastonite crystals are seen in the original surface as tiny peaks, and after soaking holes can be observed instead. The images are taken of the same surfaces and identical locations. The lines in the images show the location of the surface line profile given in Fig. 2c. Dissolution of crystals with average size less than 20 μm, i.e. typical value for crystals in floor tile surfaces, does not lead to changes in average surface roughness. However, when observing different line profiles before and after soaking, clear changes in micro-roughness of the surfaces can be verified. This indicates that the increase of micro-roughness caused by selective dissolution of the surface is the main reason for the observed differences in cleaning degree.

Cleaning degree of Glazes 11 E and 13 E before and after soaking are given in Fig. 3. In the diagram is also given cleaning degree after repeated soiling and cleaning for each surface. Formation of holes in the surface decreases cleaning degree. If the number and size of holes is large, cleaning degree will be lowered by accumulation of soil. If the holes are small, cleaning degree will be lowered

Table 2
Glaze properties gloss, surface roughness R_a and cleaning degree according to the crystalline phases observed in the surface

Property	Crystalline phases in the surface			
	Diopside	Diopside, woll.	Wollastonite	Wollastonite, pseudowoll.
Gloss, %	15–82	43–72	73–82	2–25
R_a before, μm	1.0–0.1	0.4–0.2	0.4–0.1	4.4–0.5
R_a after, μm	1.0–0.1	0.4–0.2	0.3–0.1	4.6–0.5
Cleaning before, %	75–96	85–92	91–94	2–65
Cleaning after, %	78–100	71–78	63–90	13–45

Before = original surface; after = surface soaked in slightly alkaline detergent.

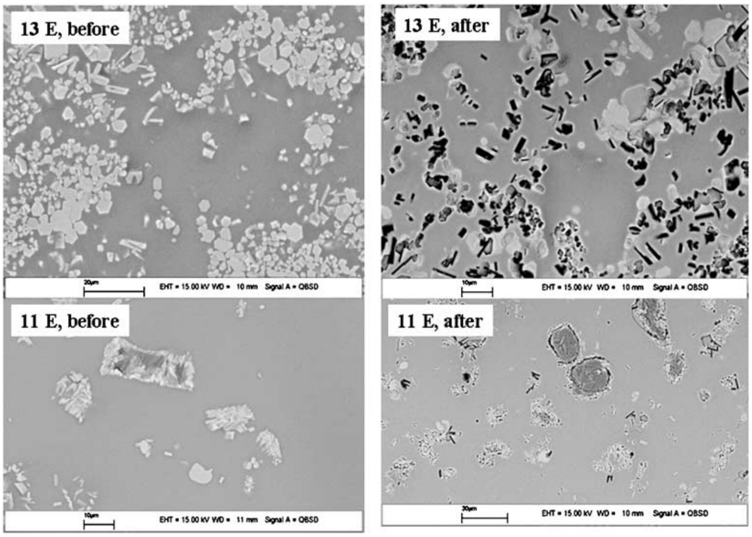

Fig. 1. SEM-images of Glazes 13 E and 11 E before and after soaking in slightly alkaline cleaning agent solution. Wollastonite (columnar crystals) and pseudowollastonite (hexagonal crystals) in Glaze 13 E partly dissolve during soaking. Wollastonite (columnar crystals) in Glaze 11 E dissolve during soaking and reveal darker quartz crystals.

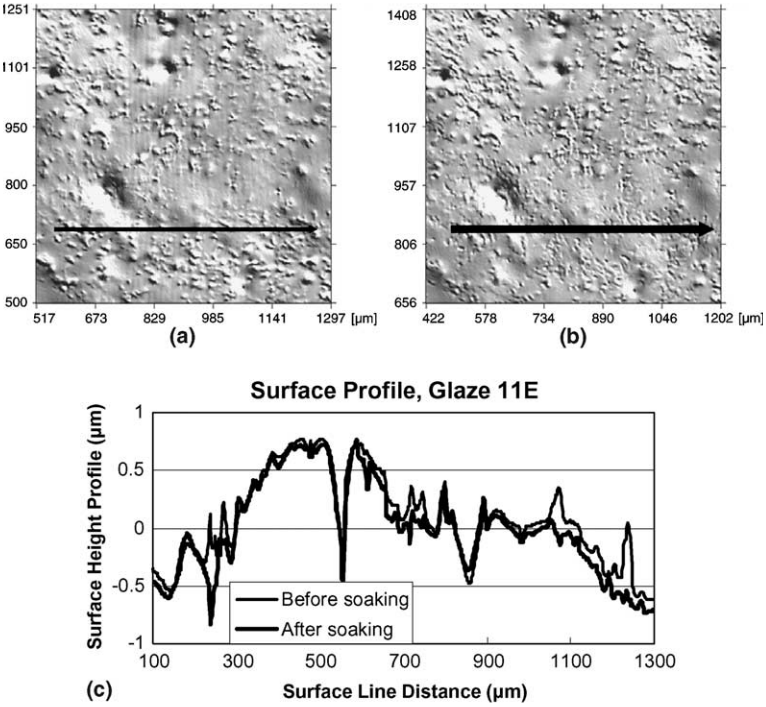

Fig. 2. COM-images of Glaze 11 E before (a), and after (b) soaking in alkaline cleaning agent solution. (c) Surface height profile of the lines indicated in (a) and (b).

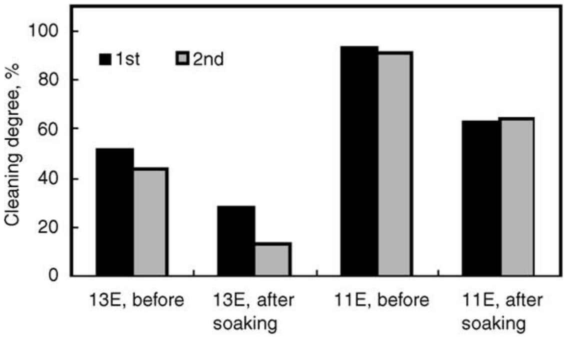

Fig. 3. Cleaning degree of Glazes 13 E and 11 E before and after soaking in alkaline cleaning agent solution. 1st, cleaning degree after first soiling and cleaning; 2nd, cleaning degree after repeated soiling and cleaning.

compared to the original surface but soil is not accumulated to any greater degree.

4. Conclusion

Soiling and cleaning degree of traditional glaze surfaces consisting of different crystalline phases embedded in a glassy phase depends rather on surface micro- and macro-roughness than on chemical composition of the phases in the surface. However, chemical durability is closely related to the crystalline phases in the surface. Wollastonite and pseudowollastonite in the surface lead to surface pitting in alkaline detergent solutions typically used for cleaning of every-day life surfaces. Surface degradation was observed to decrease cleanability and also to lead to accumulation of more soil on the surfaces. The information gained will be used to develop new glaze compositions with desired surface roughness, increased chemical resistance and cleanability.

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