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Journal of the European Ceramic Society 27 (2007) 1811–1816

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Chemical durability of glazed surfaces

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Abstract

Chemical durability of glazes is previously mostly studied as corrosion of the glassy phase. In this work the focus is on corrosion tendency of the typical crystalline phases in raw glazes. Fifteen experimental glazes were ball-milled of commercial raw materials. After fast-firing in industrial kiln and traditional firing in laboratory furnace the glazes were immersed in aqueous solutions of different pH. Changes in the phase composition of the surfaces were analysed with visual examination, XRD and SEM/EDX applying a procedure allowing to study the same crystal both before and after immersion. The results indicate that wollastonite type crystals were attacked in all but the most alkaline solutions. Diopside, quartz and corundum crystals did not show any marked attack. The interfacial layer around feldspar crystals as well as the glassy phase in the glazes corroded in the most acidic and alkaline environments.

Keywords: Grain boundaries; Interfaces; Corrosion; Glass; Glaze

1. Introduction

In general, glazes have a good chemical durability in aqueous environments except in strong acids and bases. The high alumina as well as low alkali oxide content makes glazes superior to e.g. conventional soda-lime type glasses. Time, temperature and pH of the attacking medium are the most important factors for aqueous corrosion of ceramic coatings.[1] Chemical durability of glazes in aqueous environments is often studied as durability of the glassy phase. The glassy phase is assumed to react similarly to conventional glasses, i.e. with ion-exchange of alkali ions in acidic environments. Network dissolution becomes the main mode of glaze dissolution in alkaline environments. Thus, in general the durability in alkaline environments is poor.

However, in several applications the glazed surface also contains crystalline components. Predicting the chemical durability of glazes cannot thus be based on the simple additive principles usually used for homogenous glasses. The typical crystals in glazes are mullite, anorthite and wollastonite, i.e. different silicates.[2] Literature of the behaviour of these crystals in environments where glazes are typically used is sparse. Recently, wollastonite and anorthite in glazes were reported to be attacked in acidic and neutral environments.[3–7] Dissolution kinetics of silicates has been thoroughly studied at conditions typical for geochemistry or mineral processing.[8–10] For most silicate crystals the dissolution is linear and shows strong pH dependence. The reactions are reported to initiate at grain boundaries and other imperfections in crystal structure or at impurities attached to the grain surfaces. Dissolution of wollastonite was reported to be incongruent, i.e. to have different velocities for the dissolution of calcium and silicon ions, and thus to lead to a formation of a silica gel in the surface. The dissolution studies on diopside crystals did not, however, show differences in the mutual solubility of the different components. Corrosion of crystalline albite in a glassy phase with corresponding composition indicated that albite is dissolved congruently, as the sodium ion dissolution from the glassy phase was much higher than of the other components, i.e. corresponding to a typical ion exchange reaction of glasses. Studies on corrosion of glass-ceramics indicated that the chemical durability cannot be solely deduced from the durability of the separate phases but also interfaces have to be taken into account.[11] The phase boundary attack was assumed be due to stresses or minor compositional gradients at the interface.

Chemical durability of glazes is often classified visually after exposure to different aqueous solutions according to standard methods. Visual methods are well suited for product control, and also for overall estimation of the surface quality, colour and

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doi:10.1016/j.jeurceramsoc.2006.04.162

Table 1
Compositional range (wt.%) of experimental raw glazes

Raw material range (wt.%)	
Kaolin	5–8
Feldspar	25–77
Dolomite	0–15
Limestone	0–43
Corundum	0–14
Quartz	0–49
Oxide range (wt.%)	
Na_2O	1.7–5.1
K_2O	1.4–3.9
MgO	0–6.5
CaO	6–34.3
Al_2O_3	6–16.7
SiO_2	48.5–79.2

gloss. However, visual methods fail to reveal to origin of the changes in the surface properties.[5] Also, micro-scaled changes in surface composition are not always seen in a visual inspection but can cause problems with the long-term performance of the surface, e.g. with soil attachment and cleanability of the surface.[12]

In this work chemical durability of glazes has been studied with the focus on the detailed phase composition. The goal was to compare how the type and origin of the crystalline phases affect the durability.

2. Experimental

Totally 15 experimental glazes were ball-milled of kaolin, feldspar, limestone, dolomite, wollastonite, corundum and quartz within the oxide range of interest for floor tile and sanitaryware glazes, c.f. Table 1. The exact composition of the glazes is given elsewhere.[13] The glazes were applied on green tiles in a laboratory scale by waterfall coating and fired to 1215 °C in an industrial kiln with total firing cycle of roughly 60 min and in an electric laboratory furnace with total firing cycle of roughly 24 h. Chemical durability of the glazes was tested according to the standard method ISO 10545-13. The glazes were also immersed in three cleaning agent solutions with pH-values 2.3, 9.1 and 12.0.

The influence of the crystal phase origin on the chemical durability was compared with one glaze prepared with either limestone or wollastonite mineral as lime raw material. After

Table 2
Crystalline phases identified in the samples

Fast-firing main phase	other phases	Traditional firing
DI	Q	DI
DI	Q	AN–AL, DI
DI	Q, C	KF–AL, DI
DI, WO	Q	DI
W	Q, C	AN–AL
PW, W	Q	PW, (W)

(a) Fast-firing, and (b) traditional firing. DI = diopside, Q = quartz, W = wollastonite, PW = pseudowollastonite, C = corundum, AN = anorthite, AL = albite, KF = potassium feldspar.

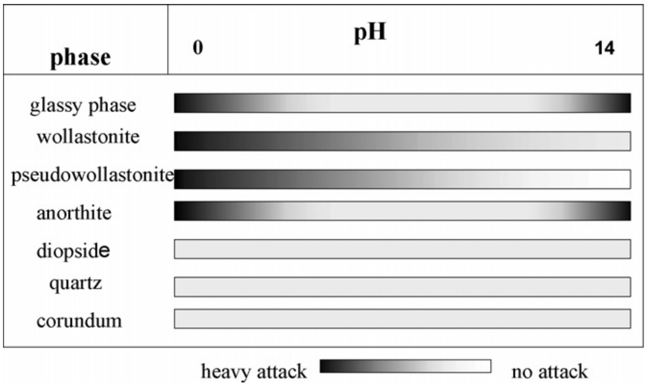

Fig. 1. Overall corrosion of different phases in aqueous solution of different pH as deduced from SEM images.

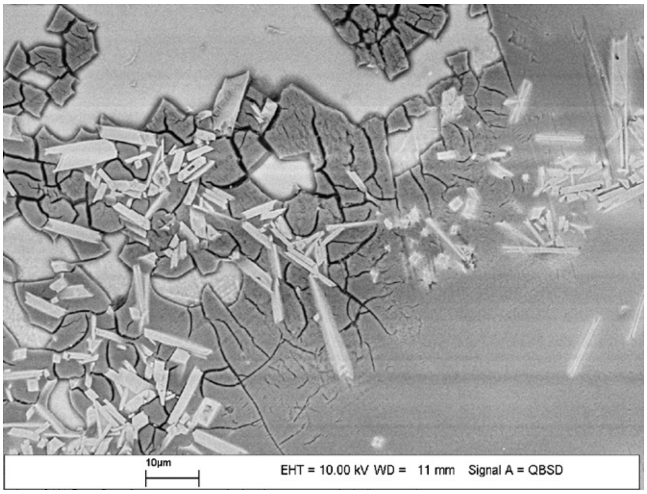

Fig. 2. SEM image of a fast-fired glaze at 4 days immersion in18% HCl. Glaze composition: Na_2O 1.9, K_2O 1.5, MgO 6.5, CaO 20.4, Al_2O_3 16.0, SiO_2 53.7 wt.%. Columnar diopside crystals and a partly peeled off silica rich glassy layer are seen.

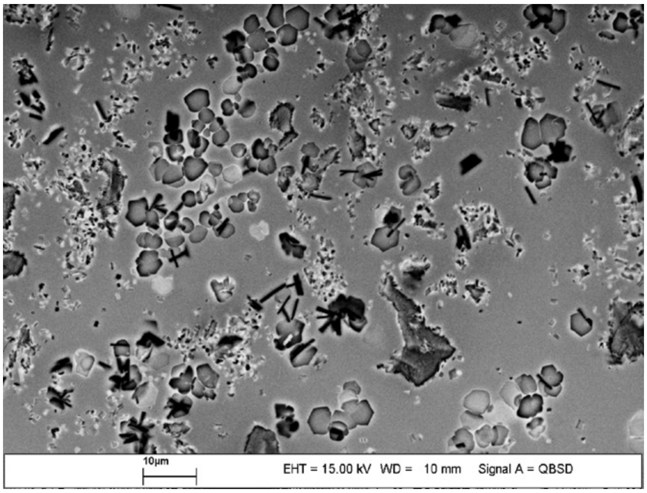

Fig. 3. SEM image of a fast-fired glaze at 4 days immersion in slightly alkaline cleaning agent solution (pH 9.1). Glaze composition: Na_2O 1.8, K_2O 1.5, CaO 19.4, Al_2O_3 6.2, SiO_2 71.1 wt.%. Quartz, columnar holes left by detached wollastonite crystals and partly dissolved hexagonal pseudowollastonite crystals are seen.

immersion the surfaces were examined visually according to the standard method. The phase composition of the surfaces were analysed with XRD (X'pert by Philips) and SEM/EDX (Leo 1530 with a Vantage EDXA from Thermo Noram).

3. Results and discussion

Phase composition of the experimental glazes strongly depends on the firing cycle, c.f. Table 2. The main crystalline components observed with the X-ray analysis in the fast-fired glazes were diopside, wollastonite and pseudowollastonite. These crystals were mainly found in the vicinity of larger quartz grains. In some glazes also corundum could be identified. When the same compositions were fired in the longer cycle, also feldspar type crystals could be identified. These crystals were predominantly plagioclase, i.e. solid solutions of anorthite and albite, but also potassium feldspar was observed in solid solution with albite in glazes with high dolomite and corundum content. The influence of the firing parameters on the phase composition is discussed more detailed elsewhere.[14] The relative amount and size of the crystals in the surfaces increases with prolonged firing. However, the relative amount of diopside decreases, and wollastonite almost totally disappears in the traditional firing. The dissolution or reaction of these crystals with corundum and

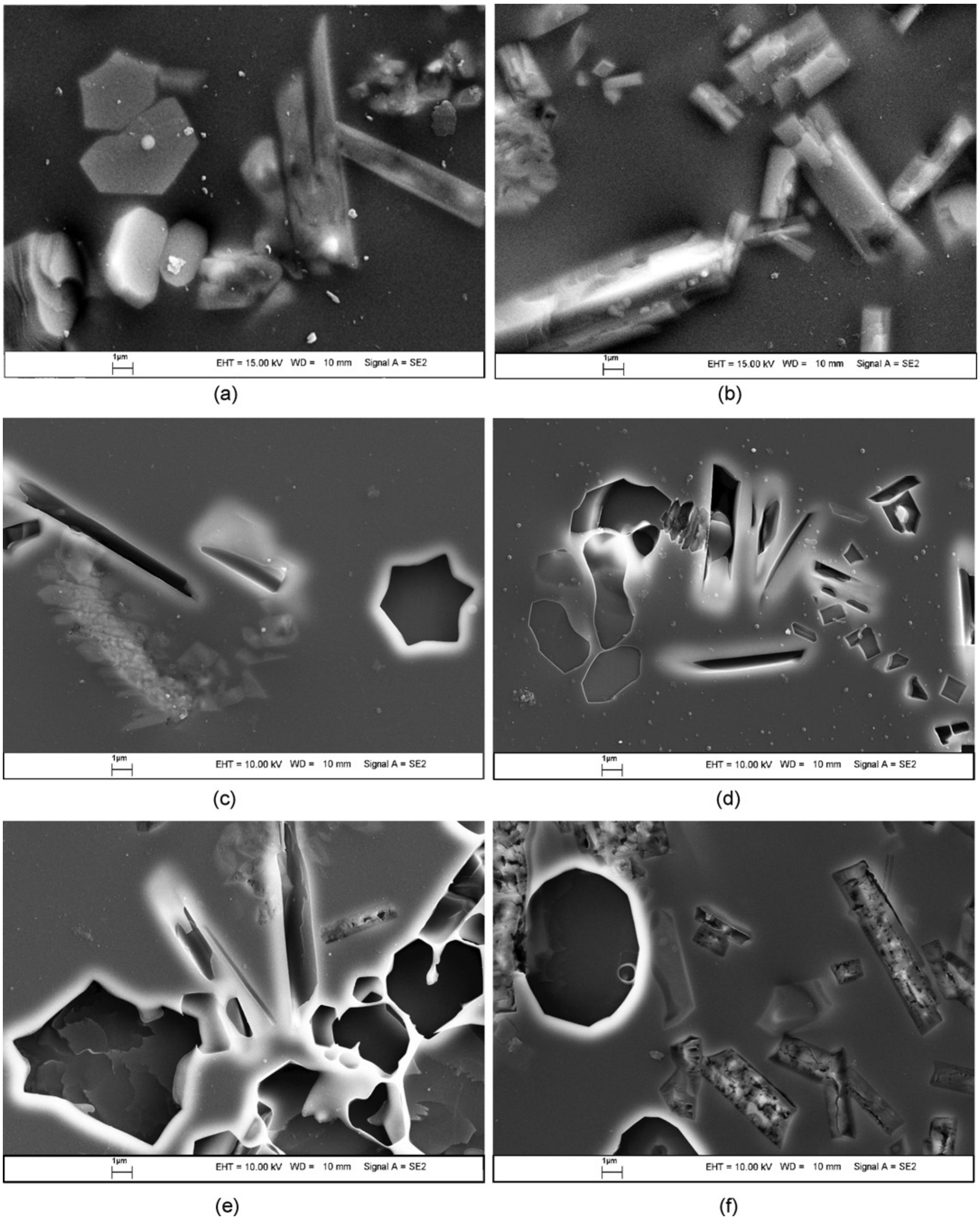

Fig. 4. SEM images of citric acid attack on I: limestone based glazes (a) reference (c) 3 h, (e) 12 h; and (II) wollastonite mineral based glazes (b) reference, (d) 3 h and (f) 12 h. Oxide composition as in Fig. 4.

the feldspar rich melt favours the precipitation of feldspar crystals during the longer maturing or post-sintering cooling of the traditional firing. Only pseudowollastonite crystals formed in the magnesia free compositions during fast firing increase in size during the longer traditional firing. The chemical reactions leading to the formation of the first intermediate crystals diopside, wollastonite and pseudowollastonite, and their further dissolution or growth is likely to give interfacial layer around them affecting the durability of the surface.

Chemical durability of the different phases after immersion in the aqueous solutions was estimated both visually and based on the SEM images. These two methods gave similar results, if the surface was severely attacked or the size of the attacked crystals was large. Selective corrosion of small crystals with dimensions of a few micrometers could be identified in the SEM images. The overall chemical resistance of the different phases as function of the pH as deduced from the SEM images is summarized in Fig. 1.

The glassy phase was attacked in strongly acidic and alkaline solutions. In the most acidic solutions ion exchange reaction of the alkalis and alkaline earths to hydrogen was observed as a formation of a silica rich layer and a partial peeling off the layer, c.f. Fig. 2. The surface of this fast-fired glaze shows columnar diopside crystals, and a partly cracked and peeled-off silica rich layer. Diopside, corundum and quartz crystals were intact after the immersion in the test solutions. Further, no interfacial attack could be observed around these crystals. This can be explained by the increased durability of the glassy phase due to dissolving alumina from corundum, silica from quartz, and the stoichiometric combination of magnesia, lime and silicate from diopside. The attack of the feldspar type crystals was mainly observed as pitting along the interfaces of the crystals or the

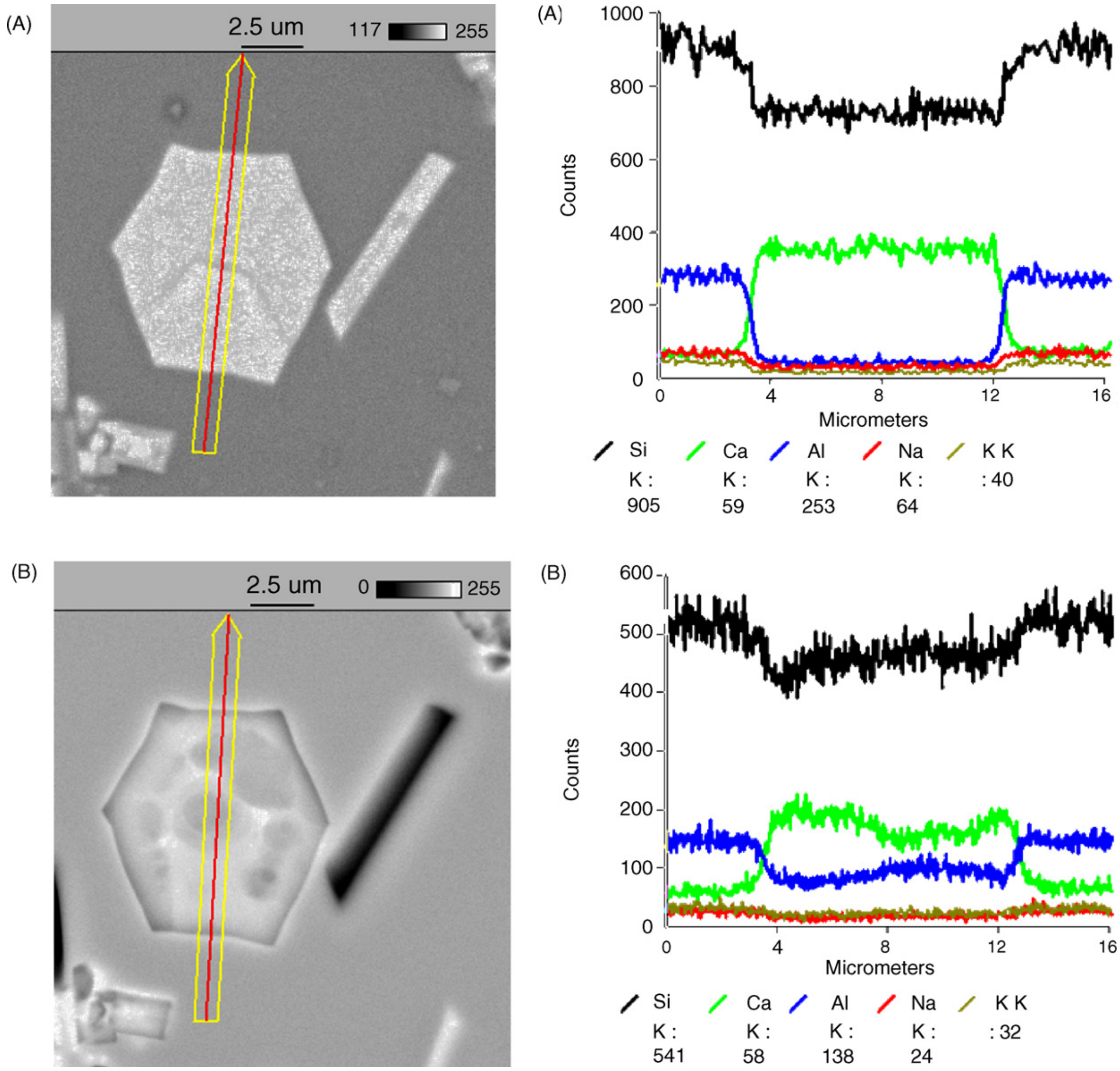

Fig. 5. SEM images and EDX line analysis of a pseudowollastonite crystal and the glassy phase before (A) and after (B) four days immersion in alkaline cleaning agent solution (pH 9.1).

glassy phase in the most acidic environments. In the alkaline solutions the attack was concentrated in the glassy phase and the crystal interfaces. Thus, the attack observed in glazes containing feldspar could depend on the formation of a thin interfacial glassy layer with lower chemical resistance than the main glassy phase. The feldspar corrosion thus obviously is due to corrosion of glassy phase, not feldspar crystals.

Wollastonite and pseudowollastonite were found to be severely attacked in all the solutions up to roughly pH 10. Fig. 3 shows a SEM image of a fast-fired surface from which most of the columnar wollastonite and some of the hexagonal pseudowollastonite crystals have been leached during the 4 days long immersion in the alkaline cleaning agent solution of pH 9.1. The influence of the origin of the wollastonite type crystals on their chemical resistance is given by SEM images in Fig. 4. The glazes have same oxide composition but contain either limestone or wollastonite mineral as the lime raw material. The limestone based glaze (Fig. 4a) contains both columnar wollastonite and hexagonal pseudowollastonite crystals formed from the reactions between limestone and quartz during firing. In the other glaze rather irregular residual wollastonite polycrystals can be seen (Fig. 4b). When the glazes were immersed in the citric acid solution (pH 1.5) the crystals started to corrode after a short exposure, if the crystal surface was not covered by a glassy phase. Also the thin glassy layer covering the crystals just underneath the surface was readily attacked. The wollastonite crystals formed during the firing reactions were severely attacked as seen by the black columnar holes in the images after an exposure of 3 h (Fig. 4c) and 12 h (Fig. 4e). The pseudowollastonite crystals have also been attacked and the sheet like structure of the crystals is now clearly seen. The attack appears to be preferentially along the lime rich planes in the crystals. Crystals originating from wollastonite mineral were also attacked preferentially along the interfacial glassy layer and also along crystal surfaces and grain boundaries (Fig. 4d and f). Thus, two types of corrosion in glazes containing wollastonite or pseudowollastonite can be observed: one of the interfacial glassy layers around the crystals and the other in the crystal surfaces, planes and boundaries. The interfacial corrosion is assumed to depend on the formation of a glassy layer of low silica and alumina content but of high lime content around the crystals. The corrosion observed in the crystal surfaces and layers is typical for the fibrous structure of wollastonite mineral and also selective leaching of lime from wollastonite.

The relative distribution between cations in one and the same sample of pseudowollastonite and the glassy phase before and after exposure to slightly acidic cleaning agent solution for 4 days is given the SEM/EDXA map in Fig. 5. The uneven corrosion of pseudowollastonite suggests corrosion along certain planes in the layer structure of the crystal so that lime is preferentially attacked. The line analysis of the ions indicates a sharp decrease in both alumina and silica content and a corresponding increase in lime content in the interfacial glassy layer around the crystal. Poor chemical resistance of the interfacial layer appears to initiate the corrosion reactions and thus revealing the crystal surface for direct attack of the aqueous solution.

4. Conclusions

Based on this work the corrosion of glazes is very sensitive to the phase composition. The crystalline phases, interfaces and glass phase behave very differently. It was shown that wollastonite and pseudowollastonite crystals are readily attacked by acidic and neutral aqueous solutions by corrosion reactions at interfaces, crystal planes and boundaries. The origin of the wollastonite crystals did not influence their durability, although the reactions in polycrystals of wollastonite mineral primarily proceeded along boundaries. Diopside, corundum and quartz crystals were found to have good chemical resistance in aqueous solutions. In glazes containing feldspar crystals the glassy phase was corroded and can thus be related with the chemical resistance of glasses. The results indicate that glazes with wollastonite type crystals in the close vicinity of or penetrating the surface have low chemical durability, and thus should be avoided. This can be implemented by proper adjustment of the glaze composition and firing conditions.

Acknowledgements

This work is part of the Activities of the Åbo Akademi Process Chemistry Centre funded by the Academy of Finland in their Centres of Excellence Programme. Financial support from the Clean Surfaces 2002–2006 Technology Programme by the Finnish National Technology Agency (Tekes), Graduate School of Materials Research, Ido Bathroom Ltd, Pukkila Oy Ab and Farmos is acknowledged. Ms Susanne Ena, Ms Jaana Paananen and Mr Clifford Ekholm are thanked for their help with the analysis of the samples.

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