CHEMICAL RESISTANCE OF FAST-FIRED RAW GLAZES IN SOLUTIONS CONTAINING CLEANING AGENTS, ACIDS OR BASES

Stina Vane-Tempest, Thomas Kronberg, Linda Fröberg and Leena Hupa

Åbo Akademi University, Process Chemistry Centre
Turku / Åbo, Finland

ABSTRACT

Chemical resistance of fast-fired raw glazes were tested in several solutions containing acids, bases or cleaning agents. The testing was done by a visual comparison according to a standard method used in tile manufacture. The surfaces were also examined with SEM for detailed information of the chemical effects of the test solutions on the glassy and crystalline phases. The visual examination fails in some cases to reveal a corrosion attack clearly seen on SEM analysis. Wollastonite and pseudowollastonite crystals were found to corrode in the test solutions. If these crystals are very small, the holes left in the surfaces after the dissolution are equally small and do not correlate with the visual experience of the surface. The corrosion of the glassy phase, especially in acidic solutions, is also seen better in the SEM examination. Cleaning agents often contain chelating compounds, which were found to affect the dissolution of the glassy phase in the glazes. The corrosion of the glassy phase was also found to be strongly dependent on the acidity of the test solution.

1. INTRODUCTION

Chemical resistance of glazed tiles is usually tested in water solutions containing one active component like an acid, base or a salt. In the standard method for tiles the glazes are divided into different classes according to a visual inspection of the surface appearance after an exposure to the test solutions[1]. The testing method does not require any special instruments and is thus suitable for everyday quality control in production. However, when developing new better compositions or studying the reason of an observed surface damage more accurate methods are needed. The visual classification can be improved by studying the corroded glazes with different surface sensitive methods like SEM, AFM and XRD[2].

Most of the corrosion studies reported in literature deal with tableware ceramics or glasses[3, 4]. Corrosion of glazes is a complicated process as the surface often consists of both a glassy phase and one or several different crystalline phases. The chemical resistance of the glassy phase can be described analogously to the corrosion of silicate glasses[5, 6]. Corrosion of glasses is usually described as leaching of alkalis by ion exchange in acidic solutions. The rate of the process is controlled by the diffusion rate of the ions, and decreases with time. In alkaline solutions a complete dissolution of the glass network takes place at a constant rate[6 - 11]. The influence of the chemical composition on the resistance commercial soda-lime type glasses is widely studied[12 - 16]. However, a basic understanding of the behaviour of glazed surfaces in different environments is still incomplete.

In everyday life the tile surfaces are cleaned with cleaning agents containing mixtures of different surface-active components, chelating agents, soaps and acids or bases. If the normal washing leads to e.g. selective dissolution of some components from the surface, the soiling resistance will be changed. In this work the chemical resistance of some fast-fired raw glazes in different solutions of acids, bases and salts was compared with their resistance in three model cleaning agent solutions. The influence of the phase composition on the chemical resistance of the surface is examined. We also compare the results based on the visual examination with the signs of attack observed in SEM-analyses. Further, we study whether the chemical resistance measured in solutions containing only one active component could be used to estimate the chemical resistance of the glazes in typical cleaning agents used in everyday life.

2. EXPERIMENTAL

Four different raw glaze compositions were studied in this work. The oxide composition of the glazes is given in Table 1. The glazes were mixed of commercial grade raw materials of dolomite, whiting, feldspar, corundum, kaolin, and quartz. The fines of the raw materials were chosen so that the 10 % of the particles have a size less than 25 μm. The suspensions were milled in a fast laboratory ball mill, and the particle size distribution was controlled with a Sedigraph. The glaze suspensions were waterfall-coated in laboratory scale on green tile bodies. The viscosity of the glaze suspensions, the amount of the glaze mixture on the tile, and the speed of the glazing line were controlled during the glaze application. The tiles were fired in an industrial roll kiln with a firing cycle of 55 minutes and a top temperature of 1215°C. The water absorption of the tiles was tested according to ISO 10545-3. For the experimental tiles the accepted water absorption is less than 0.5 %.

Oxide (wt%)	A1	A2	A3	A4
CaO	17.5	17.4	5.5	17.5
$Na_2O + K_2O$	4.1	4.0	3.9	7.0
SiO_2	49.4	64.5	77.1	56.0
Al_2O_3	25.0	10.1	9.9	17.5
MgO	4.0	4.0	3.7	2.0
Raw material comp. (wt%)				
Feldspar	26.0	26.2	27.2	48.0
Kaolin	8.0	8.0	8.0	8.0
Dolomite	15	15	15.4	7.4
Corundum	13	0.3	0.6	3
Chalk	17.8	17.7	0	22.1
Quartz	20.2	32.8	48.8	11.6
GLOSS	34.1	42.5	15.2	82.4

Table 1. The oxide and the raw material compositions of the experimental glazes in wt%.

The resistance of the glazes in different water solutions containing acids and bases was determined according to the method described in the standard ISO 10545-13[1]. The chemical resistance of the glazes was also tested in one acidic, one alkaline, and one weakly alkaline cleaning agent according to the same procedure. The exposure time for the testing of resistance in cleaning agent solutions was four days. The acidic cleaning agent contains citric and gluconic acid. Sodium metasilicate pentahydrate is the active component in the alkaline cleaning agent. This solution also contains a non-ionic surfactant. The weakly alkaline cleaning agent contains soap and a non-ionic surfactant. The test solutions were diluted according to normal cleaning agent recommendations to 3 vol% solutions.

The visual method described in the standard test ISO 10545-13 only classifies the surfaces into three different categories according to a more or less subjective experience. To achieve a more accurate description of the chemical resistance the surfaces were also studied with SEM-EDXA (LEO Electron Microscopy LTD S360).

3. RESULTS AND DISCUSSION

The corroding effect of the standard test solutions and the cleaning agent solutions on the experimental glazes is given in Table 2. The solutions are listed in the table according to their increasing pH-value. According to the standard method the visible signs of attack divide the surfaces into three classes: A with no visible effect, B with definite change in appearance, and C with partial or complete loss of the original surface. When the surfaces were examined with SEM, the visual signs of attack could always be verified. However, in some test solutions different degrees of corrosion were observed, also in cases where visual examination did not reveal any signs of attack. This means that the visual examination can be unreliable. The method is also sensitive to the experience of the observer. A corrosion not revealed to the naked eye might influence the long-time chemical resistance and the soiling and cleaning properties of the surface. The observations from the SEM-analyses are divided into four classes, i.e. no signs of attack, some signs of attack, clear attack, and severe damage.

Test solution		Glaze A1		Glaze A2		Glaze A3		Glaze A4	
Composition	pH	Visual	SEM	Visual	SEM	Visual	SEM	Visual	SEM
Hydrochloric acid 18 %	-0.9	C	+++	A	+++	A	++	B	+++
Hydrochloric acid 3 %	0.3	C	+	A	++	A	+	B	++
Citric acid	1.5	A	+	A	+	A	-	B	+
Lactic acid	1.7	C	++	A	++	A	+	B	++
Acidic cleaning agent	2.3	A	+	A	+	A	+	A	++
Ammonium chloride	5.0	A	-	A	-	A	-	A	++
Sodium hypochlorite	9.0	A	-	A	-	A	-	A	-
Weakly alkaline cleaning agent	9.1	A	-	A	++	A	+	B	++
Alkaline cleaning agent	12.0	A	-	A	-	A	-	A	++
Potassium hydroxide 3%	13.4	A	+	A	+	A	-	A	++
Potassium hydroxide 10 %	14.0	A	++	A	++	C	+	A	++

Table 2. Attack of the test solutions to the experimental surfaces according to a visual examination: A = no visible effect, B =definite change in appearance, C =partial or complete loss off the original surface[11]. Estimation of attack from SEM-images: +++ severe attack, ++ clear attack, + signs of attack, and – no signs.

The SEM-images of the reference surfaces and the surfaces exposed to the standard test solutions, hydrochloric acid (18%), citric acid and potassium hydroxide (10%), and to two cleaning agent solutions are given in Figures 1–4. The phase composition of the experimental glazes is given in Table 3. The development of the crystalline phases as well as their identification is discussed in another paper[17].

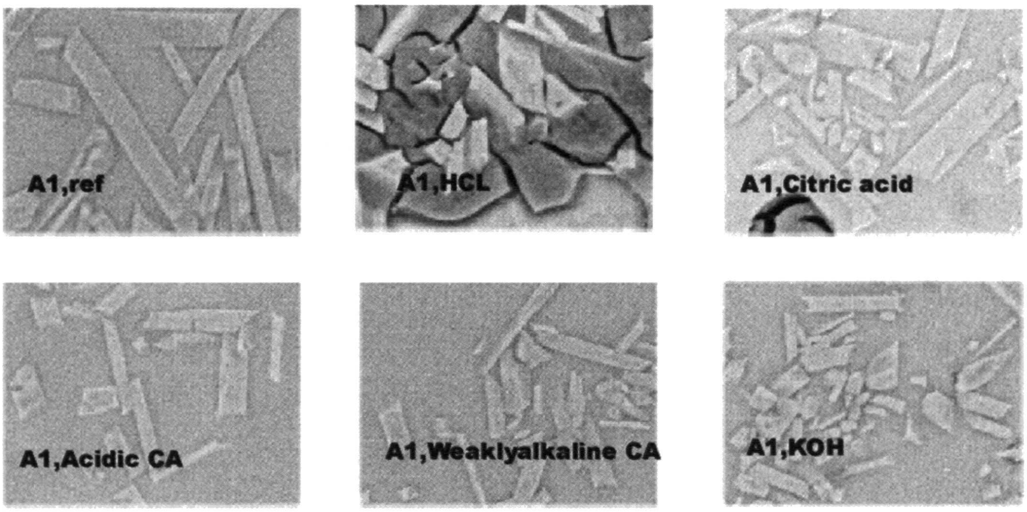

Figure 1. SEM-images of the surface of Glaze A1 before and after exposure to different test solutions as specified in the images. CA=cleaning agent

Glaze A1 shows clear attacks of corrosion in the most acidic solutions when examined visually. The SEM images reveal that the diopside crystals in the surface are intact but the glassy phase has corroded severely in the strong HCl-solution. The exposure to the HCl-solution leads to a layer with several cracks. According to SEM-EDX analysis this layer consists of silica. This indicates that the alkalis from the glassy phase have leached out and been replaced by hydrogen ions. This reaction leads to silica gel formation on the surface. When this water containing gel dries typical cracks are formed. Here and there the layer is peeled off.

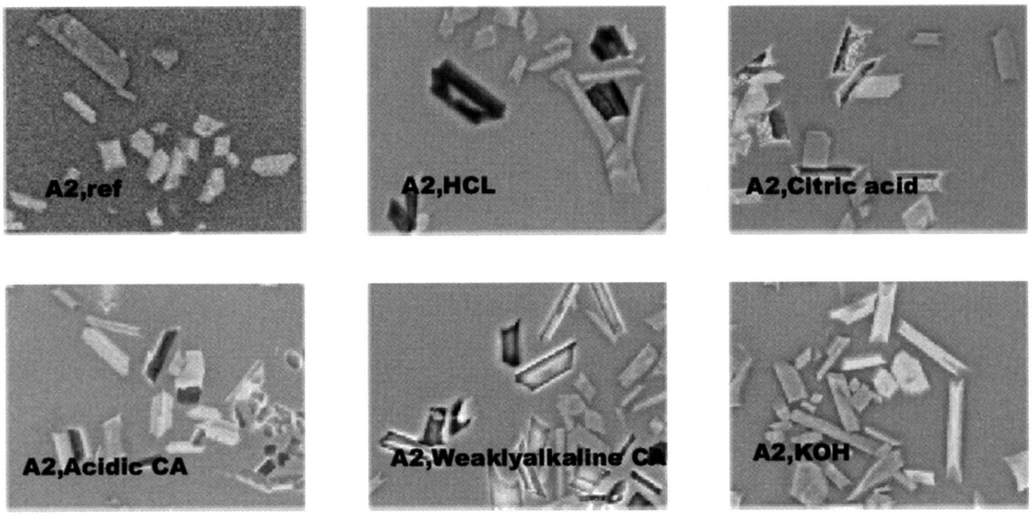

Figure 2. SEM-images of the surface of Glaze A2 before and after exposures to different test solutions. CA=cleaning agent

The exposure to the other acidic solutions excluding ammonium chloride leads to lower degree of corrosion. The signs of corrosion are seen as a hazy and spotted glassy surface. In the surfaces exposed to the most alkaline solutions the borders of the diopside crystals are more pronounced indicating that the glassy phase has started to corrode. However in the visual test the corrosion was not revealed. AFM of the unexposed surface of Glaze A1 indicates that diopside crystals have smooth surfaces, and their borders form distinct thresholds in the glassy phase[17]. However, if the corrosion of the glassy phase is slight, the visual signs of corrosion are likely to be minimal. The observations of the surface of Glaze A1 with its low silica content and thus low chemical resistance in acidic environments are consistent with the common theories and experimental results of the corrosion of glassy surfaces[6-10]. The acid resistance of glazes is increased by silica and by moderate amounts of alumina, while magnesia, lime and alkalis decrease the acid resistance[6]. The signs of attack by the less concentrated hydrochloric acid solution were roughly of the same type than those by citric and lactic acid, and by the acidic detergents. Thus the chelating components in the test solutions seem to give a more severe corrosion than simple acids of roughly the same pH. However, the pH level also is important for the corrosion intensity.

When alumina is decreased by increasing the silica content, the acid resistance of the glaze should be improved. Glaze A2 in Figure 2 shows that the increased silica content does not give as severe signs of attack of the glassy phase as in Glaze A1. According to the visual examination the chemical resistance of Glaze A2 is good. However, some signs of corrosion of the glassy phase were observed in SEM-images of the surfaces exposed to the acidic and basic solutions. Also in this case the corrosion is assumed to depend on the ion exchange reaction in acidic solutions, and the dissolution of the silicate network in the alkaline solutions. In the surface of Glaze A2 also wollastonite crystals can be observed. These crystals are clearly attacked by all but the strongest alkaline test solution.

	GLAZE A1			GLAZE A2				GLAZE A3				GLAZE A4			
	Diopside	Quartz	Glassy phase	Diopside	Wollastonite	Quartz	Glassy phase	Diopside	Glass y phase 1 (low SiO_2)	Quartz	Glassy phase 2	Wollastonite	Pseudowollastonite	Quartz	Glassy phase
HCl 18%	O	O	☒	O	☒	O	☒	O	☒	O	☒	☒	☒	O	☒
Citric acid	O	O	☒	O	X	O	☒	O	X	O	O	☒	☒	O	O
Acid cleaning agent	O	O	X	O	X	O	☒	O	☒	O	O	☒	☒	O	☒
Weakly alkaline cleaning agent	O	O	O	O	☒	O	O	O	O	O	O	☒	☒	O	☒
KOH 10 %	O	O	☒	O	O	O	☒	O	☒	O	☒	O	O	O	☒

Table 3. Corrosion of different components observed on the surfaces. O= no corrosion, X= partial corrosion, ☒ = severe corrosion

Wollastonite mineral is known to be soluble in acidic solutions. Non-reacted wollastonite crystals in the surface of fast- fired raw glazes are corroded in acidic solutions[2].

Glaze A3 contains a high content of silica added to the mixture as quartz. In fast firing the reaction and dissolution of quartz are incomplete and the glaze surface is characterized by non-reacted quartz particles and tiny diopside crystals. The visual examination gives clear signs of corrosion only in the highly alkaline test solution. SEM-images reveal some clear spots of corrosion. The glassy phase of the surface is inhomogeneous and is likely composed of alumina rich and silica rich regions. The alumina rich glassy phase is assumed to corrode in the test solutions. The corrosion of the alumina rich glassy phase is assumed to depend mostly on its low silica content and thus low chemical resistance. The glassy phase with higher silica content shows signs of corrosion only in the most acidic and alkaline solutions. This indicates that the silica content also in this glassy region is too low to give a good resistance in highly acidic and alkaline environments. In Glaze A3 quartz and diopside crystals can be seen clearly in the surface after the alkaline exposure. The tiny seeds on quartz particles have disappeared, likely due to the corrosion of a thin glassy phase surrounding the diopside crystals on the quartz particles. In a traditional firing this glaze is likely to give a much better chemical resistance.

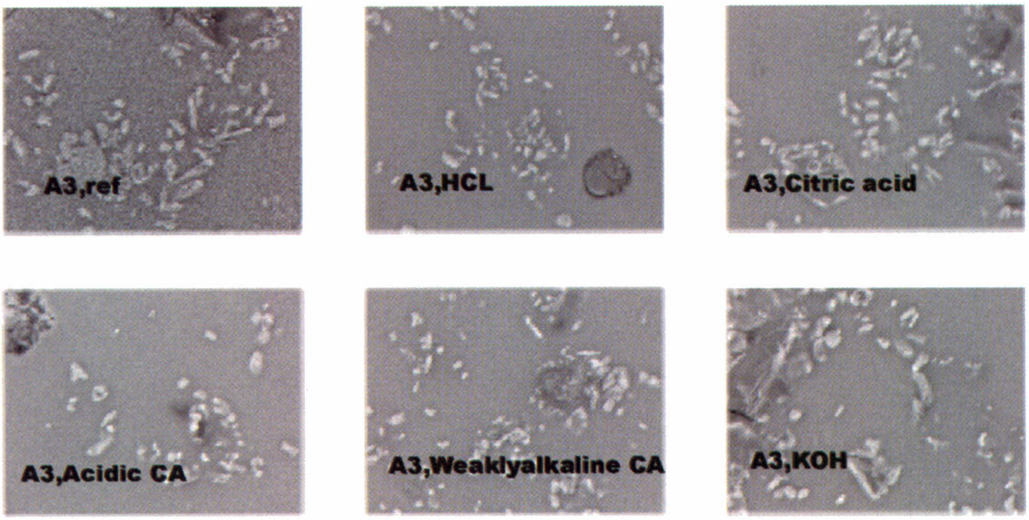

Figure 3. SEM-images of Glaze A3 before and after exposures to different test solutions. CA=cleaning agent

The raw material mixture of Glaze A4 contains a high content of feldspar and low content of quartz. In the surface a few residual quartz particles can still be seen. The other crystals identified on the surface are wollastonite and pseudowollastonite. The visual examination suggests signs of attack in some test solutions. The SEM images reveal that only in the sodium hypochlorite solution corrosion could not be detected. Both wollastonite and pseudowollastonite crystals were attacked. The glassy phase is also attacked in most solutions, again likely due to its low silica content.

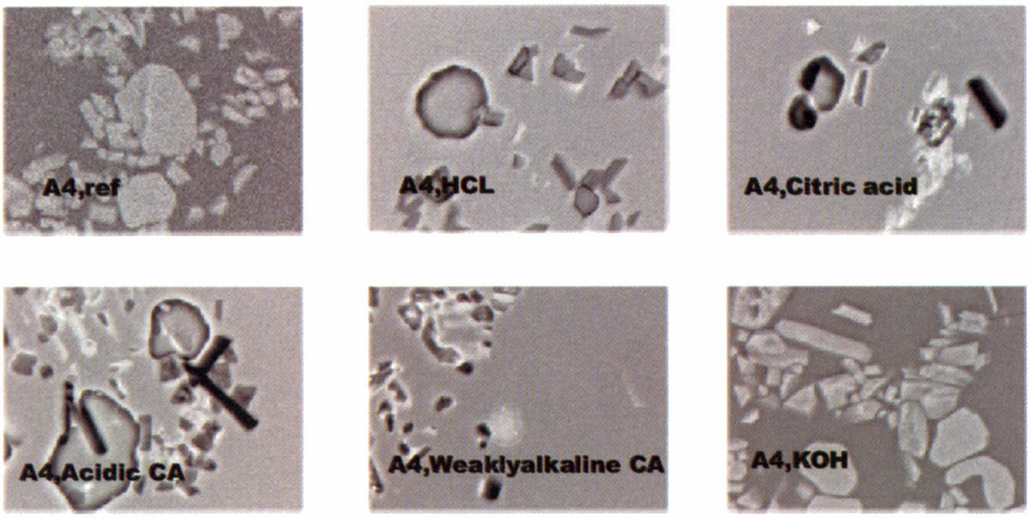

Figure 4. SEM-images of Glaze A4 before and after exposures to different test solutions. CA=cleaning agent

4. CONCLUSIONS

The chemical resistance of mat glazes in different solutions containing cleaning agents, acids or bases depends on the phase composition of the surface. In fast-firing of raw glazed tiles diopside, wollastonite and pseudowollastonite crystals are formed depending on the initial raw material composition. Also some non-reacted quartz is often identified in the surfaces[17]. The glassy phase can also be inhomogeneous. The different crystalline and glassy phases behave differently in water solutions containing different acids, bases or cleaning agents. A selective dissolution can affect the soiling resistance of the glaze, and thus make some specific compositions less attractive for certain applications.

Diopside crystals do not show any signs of corrosion when studied with SEM. However, wollastonite and pseudowollastonite crystals in the glaze surfaces corrode both in acidic and alkaline solutions. Only in concentrated alkaline solutions these crystals are likely to be chemically stable. The corrosion of these crystals is clearly seen as holes in SEM images of the glaze surfaces. The glassy phase shows clear signs of attack in acidic environments if it has low silica content. In highly alkaline solutions the glassy phase is also corroded. In acidic glasses an ion exchange reaction of the alkalis and alkaline earths to hydrogen is detected in the surface layers. If the silica content of the glassy phase is low, formation of silica gel is clearly observed. In a dry silica gel layer cracks are formed, and a peeling off can take place. In highly alkaline glasses the glassy surface is dissolved. The corrosion of the glassy phase in glazes thus follows the common principles for the corrosion of silicate glasses[10].

The standard method of testing the chemical resistance of glazed tiles notes changes in the surface appearance after exposure to the test solutions. The estimation of the changes is done visually and thus the result is only approximate. However, very often the corrosion is only of micro-scale, which does not yet show in the simple standard testing method. Thus, the visual classification applied in the standard testing method can in some cases give misleading interpretations.

The test solutions containing chelating components seem to be more corrosive to the glassy phase than simple acid solutions of the same pH without chelating compounds. Thus the cleaning agents containing e.g. citric acid or other chelating compounds might increase the corrosion of the glassy phase in glazes with relatively low silica contents. When developing the basic understanding needed for improving the corrosion resistance of glazes the behaviour of the different phases in different environments should be examined with several surface specific methods.

5. ACKNOWLEDGEMENTS.

This work is a part of the activities at Åbo Akademi Process Chemistry Centre, a National Centre of Excellence nominated by the Academy of Finland. The financial support from the Finnish National Technology Agency (Tekes) Programme Clean Surfaces 2002-2006 and the Graduate School of Materials Research are gratefully acknowledged. The work has also been supported by Ido Bathroom Ltd, Pukkila Oy Ab and Farmos. Ms Jaana Paananen and Mr Clifford Ekholm are thanked for their help with preparation and SEM-analyses of the samples.

REFERENCES

[1] International standard, ISO 10545-13 Ceramic tiles part 13; Determination of chemical resistance

[2] Kronberg, T., Hupa, L., Fröberg, K., Durability of Mat Glazes in Hydrochloric Acid Solution, 8th European Ceramic Society symposium 2003.

[3] Aubay, E., Perrin, E., Dupuy, P., Glass Corrosion in Automatic Dish Washing, 39th International Detergency Conference 1999.

[4] Buchmeier, W., Andree, H., Jeschke, P., Härer, J., Sorg, R., Untersuchungen sur Spülgutkorrosion beim

maschinellen Geschirrspülen., SÖFW-Journal, 122, nr 6, 1996, 398-405.

[5] Karlsson, S., Kemisk Beständighet och Hydrofobering av Glas och Glasyrer, KeramRapport 97-1, Swedish Ceramic Institute 1997.

[6] Carlsson, R. Korrosion av Glasyrer, 99-3tk, Swedish Ceramic Institute 1999.

[7] Ezz-Eldin,F.M.;Nageeb W.M.;Chemical resistance of some irradiated ceramic-glazes, Indian Journal of Pure&Applied Physics,Vol 39,514-424,2001

[8] Escardino A.,Amoros J.L.,Gozalbo A.,Orts ..,Lucas F.,Belda A.: Interaction between glaze layers during firing.Chemical resistance of the resulting glazes, General Conferences,Papers,Posters,Round table 1.201-217,Qualiceer,Spain 2002.

[9] Bunker, B.C., Molecular Mechanisms for Corrosion of Silica and Silicate Glasses, J. Non-Cryst. Solids, 179, 1994, 300-308.

[10] Hench, L., Clark, D.E., Physical Chemistry of Glass Surfaces, J. Non-Crys. Solids, 28, 1978, 83-105.

[11] Dietzel, A., Emaillierung, Springer-Verlag, Berlin 1981.

[12] Linzander, S., Simmingsköld, B., "Försök att eliminera eller minska behov av handdiskning inom manuell glasindustri", Glastek. Tidskr. 37 1982, 9-18.

[13] Lakatos, T., Simmingsköld, B., Glaskomponenters inverkan på glasets vattenresistens, Glastek. Tidskr. 27 (5-6) 1972, 77-80.

[14] Dilmore, M.F., Clark, D.E., Hench, L.L., Chemical Durability of Na_2O-K_2O-CaO-SiO_2 glasses, J.Am.Ceram.Soc. 51 (9-10) 1978, 439.443.

[15] Lakatos, T., Johansson, L-G., SiO_2-Al_2O_3-Na_2O-K_2O-CaO-MgO –systemets viskositet, likvidustemperatur och hydrolytiska resistens, Glastek. Tidskr. 31 1976, 31-35.

[16] Ohta, H., Suzuki, Y., Chemical durability of glasses in the systems SiO_2-CaO-Na_2O-RmOn, Am. Ceram. Soc. Bull. 57 1978, 602-604.

[17] Fröberg, L., Vane-Tempest, S., Hupa, L., Surface Composition and Topography of Fast-fired Raw Glazes, Submitted for Qualicer 2004.