CHEMICAL ETCHING AS ANTI-SLIP TREATMENT ON PORCELAIN STONEWARE TILES

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ABSTRACT

Commercial acid-based anti-slip treatments are useful to reduce the risk of slipping on ceramic tiles. Several works deal with this topic in terms of consumer safety, without studying in-depth the ceramic surface characteristics and by measuring the slip resistance with empirical methods (not standardized).

In the present work, the impact of a chemical anti-slip treatment on the surface properties of glazed ceramic tiles was investigated in terms of microstructural characteristics, gloss variations, and chemical and stain resistance. Slip performances were evaluated according to the most widespread standards. By the comparison of the treated and untreated surfaces of the same product, it was possible to analyse the effects in terms of visual appearance, cleanability and anti-slip performance.

1. INTRODUCTION

Porcelain stoneware is a product in which the synergy between manufacturing technology and physical-mechanical properties is particularly well developed with excellent results. Since this product has excellent technical characteristics, such as good flexural strength, resistance to surface abrasion and stains, surface hardness and, in comparison with other classes of tiles, a high fracture toughness, it can be used in those environments where high performance and reliability are required. For these reasons, porcelain stoneware tile production is still quite high. For example in Italy, in 2012, on a total tile production of about 367 million m^2, more than 288 million m^2 was porcelain stoneware (192 million m^2 glazed and 96 million m^2 unglazed) [1].

With the aim to reduce the risk of slipping on ceramic tiles, several treatments have been introduced to the market. Most of these treatments consist of acid based applications on the ceramic surfaces (hydrofluoric acid, ammonium bifluoride), which are able to produce chemical etching. In the literature, some works on chemical etching as anti-slip treatment are available only for glazed ceramic tiles [2,3]. These works face the problem from a consumer point of view, in terms of safety, without considering the ceramic surface characteristics. Nevertheless, studies to assess the effectiveness of the treatment in accordance with standardized methods for slip resistance are still unavailable.

Systematic investigations from the standpoint of the manufacturer, by studying in-depth the ceramic surface, are lacking.

It is indubitable that a deep knowledge of the tile characteristics, in terms of composition and microstructure, plays a key role in assessing whether the acid treatment will give rise to an anti-slip surface without damaging the ceramic product. In the literature, many works deal with the microstructural modification of glazed tiles in acid or basic environment [4,5,6,7,8] and it is known that some kinds of crystals, such as wollastonite, are corroded by hydrofluoric acid [5,9].

When commercial hydrofluoric acid- or ammonium bifluoride-based treatments are applied on the ceramic surface, several effects could be produced, such as microstructural modifications, decreased gloss, colour changes and, maybe, lower cleanability.

In the present work two commercial glazed porcelain stoneware tiles were considered and analysed before and after the anti-slip treatment, in order to correlate their performance (slip resistance, chemical and stain resistance, wettability and gloss) with their mineralogical composition and microstructural characteristics.

2. EXPERIMENTAL

Two glazed tiles having different surface finishes were considered: sample A, characterized by a heterogeneous and textured surface, and sample B with a homogeneous and smooth surface.

The commercial anti-slip treatment consists of a hydrofluoric acid-based solution, which was applied following the manufacturer's instructions: by hand, 1 minute for sample A and 30 seconds for sample B.

The photographs of both the samples before and after the acid etching are shown in Fig. 1.

Mineralogical composition and microstructural characteristics of the tile surfaces have been investigated in-depth by X-ray diffraction (PW 3830; Philips, NL) and scanning electron microscope (SEM, Zeiss EVO 40, D) equipped with an energy dispersive X-ray attachment (Inca, Oxford Instruments, UK). Surface metrology of the tiles has been studied by a confocal profiler (Leica, DCM 3D,D).

To evaluate the treatment effectiveness, on both the treated and untreated surfaces, slip resistance was determined according to several standardized methods: ramp (DIN 51130 and DIN 51097), pendulum (EN 13036-4), dynamometer (ASTM C1028) and Tortus (B.C.R.).

The effects caused by the treatment on the surface were studied in terms of stain resistance (ISO 10545-14), chemical resistance (ISO 10545-13), wettability (measurements of contact angle) and gloss variations (ASTM C346).

a

b

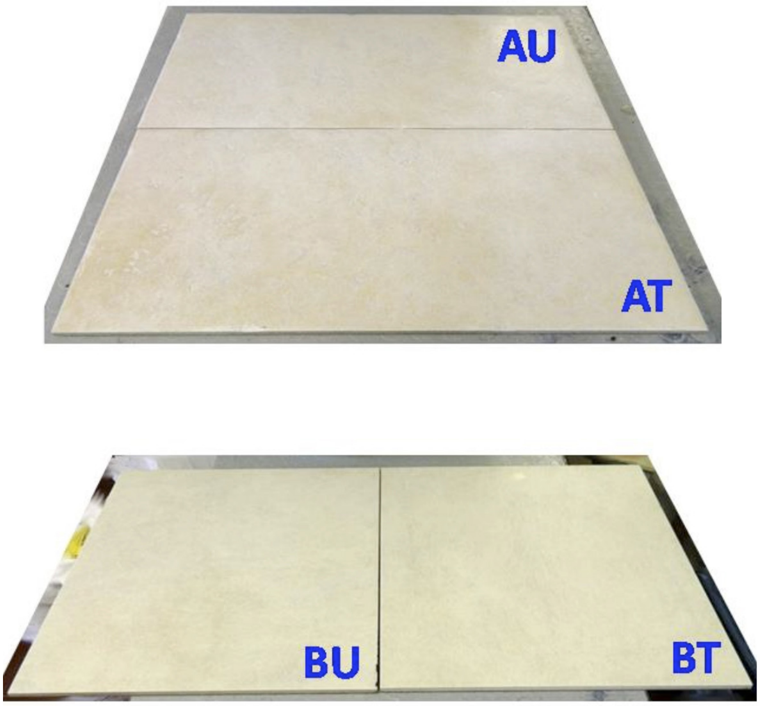

figure 1. Photos of sample A (a), untreated (AU) and treated (AT) of 30x60 cm sizes, and sample B (b) untreated (BU) and treated (BT) of 60x60 cm sizes.

3. RESULTS

The chemical (Fig. 2 of EDS spectra) and mineralogical (Table I) compositions of the untreated samples A and B do not show significant differences even if their surface finish is quite different: heterogeneous and textured for sample A and homogeneous and smooth for sample B. Plagioclase and zircon are the main crystals embedded in a glassy phase. Sample A, the textured one, shows the presence of barium in the amorphous phase and Sample B, the smoother one, shows the presence of α-alumina crystals, in traces.

After the acid treatment, the glazes still have the same overall chemical and mineralogical composition.

In sample A, the textured one, at relatively high magnification (50x objective), both the SEM micrographs (Fig. 3) and the confocal 3D images (Fig. 4 a-b), show a different microstructure before and after the treatment. The acid treatment causes a chemical etching on the ceramic surface: the amorphous phase is corroded [7,8,1] and plagioclase crystals are clearly visible on the surface. Observing larger areas of both the surfaces, treated and untreated, with the confocal profiler by using a 10x objective, only few differences are visible (Fig. 4 c-d). In particular, the treated surface seems to have lower peaks. In any case, the 3D parameters do not clearly show a tendency to higher or lower values (Table II). It is probably due to the heterogeneity and texture of the surface which could mitigate the treatment effects in terms of roughness.

Also in sample B, the smoother one, both the SEM images (Fig. 5) and the surface mapping (Fig. 6 a-b) reveal a chemical attack induced by the treatment. The acid corrodes the amorphous phase leaving zircon and plagioclase crystals clearly evident [7,8]. The surface mapping of larger areas acquired by 10x objective (Fig. 6 c-d), reveals some morphological differences after the treatment, which are once again confirmed by SEM micrographs (Fig. 5) due to the corrosion of the amorphous phase. This is highlighted by the contour diagrams (Fig. 7), in which the coloured lines join the points at the same level.

The 3D roughness parameters (Table III) confirm some differences: for the treated surface, BT, all the values are lower with respect to those of the untreated surface, BU.

Sample	Mineralogical phases
AU	Plagioclase and zircon (traces) in amorphous phase
BU	Plagioclase, zircon and α-alumina (traces) in amorphous phase

Table I. mineralogical composition of the untreated samples A and B.

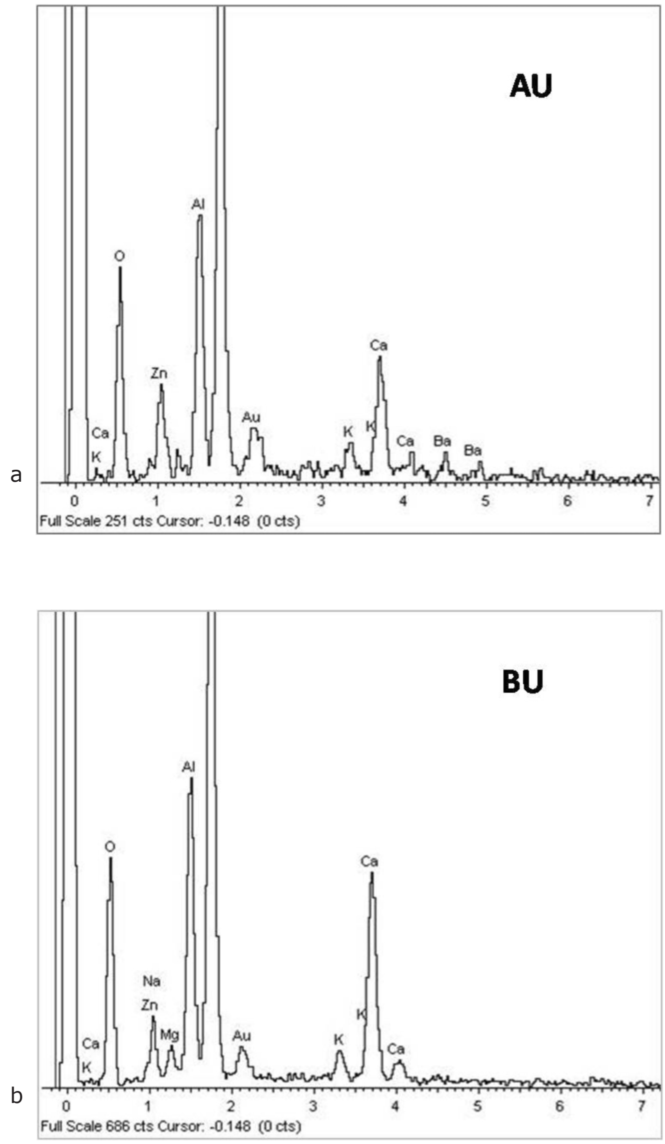

Figure 2. EDS spectra of surface areas for the untreated samples A (a) and B (b).

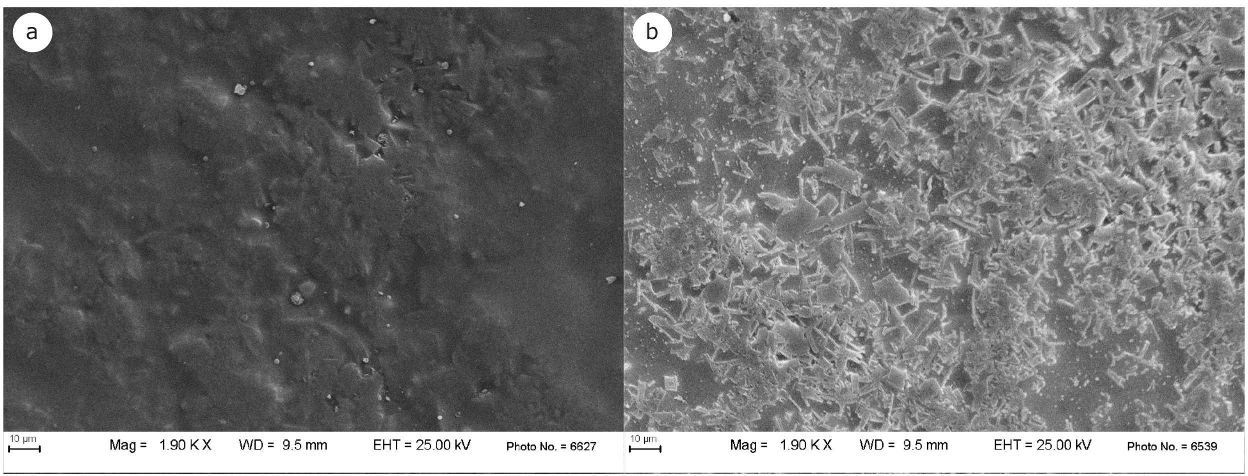

Figure 3. SEM micrographs of the untreated (a) and treated (b) sample A.

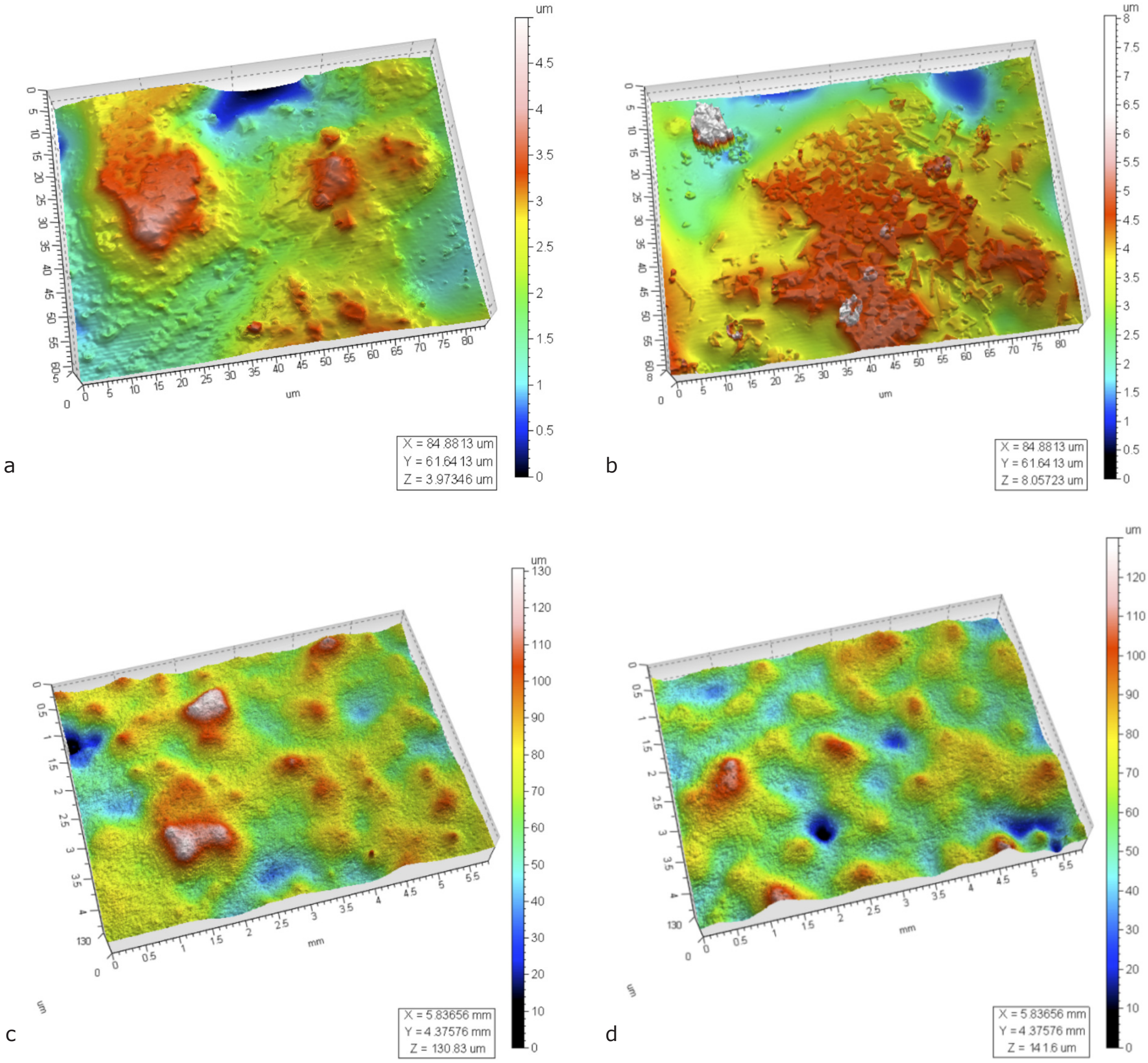

Figure 4. Confocal 3D images of sample A by using 50x objective, untreated (a) and treated (b); and by using a 10x objective, untreated (c) and treated (d).

ISO 25178 - Height Parameters -		AU	AT
S_P (mm)	Maximum peak height of the Scale Limited Surface (SLS)	62.52	82.14
S_v (mm)	Maximum pit height of the SLS	74.41	65.34
S_z (mm)	Maximum height of the SLS (sum of S_P and S_v)	136.93	147.49
S_A (mm)	Arithmetical mean height of the SLS	12.06	11.05

Table II. 3D roughness parameters of the untreated and treated sample A.

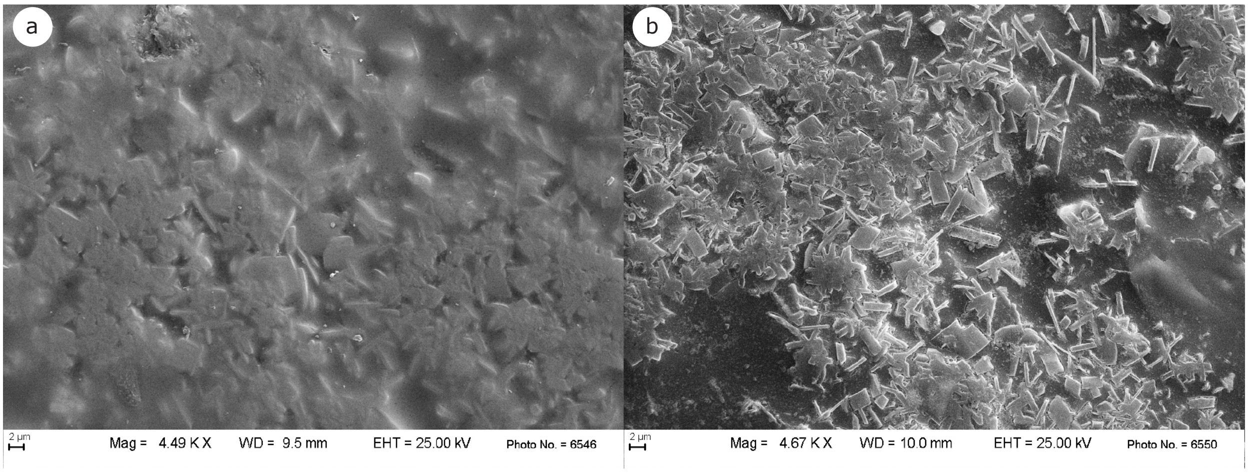

Figure 5. SEM micrographs of the untreated (a) and treated (b) sample B.

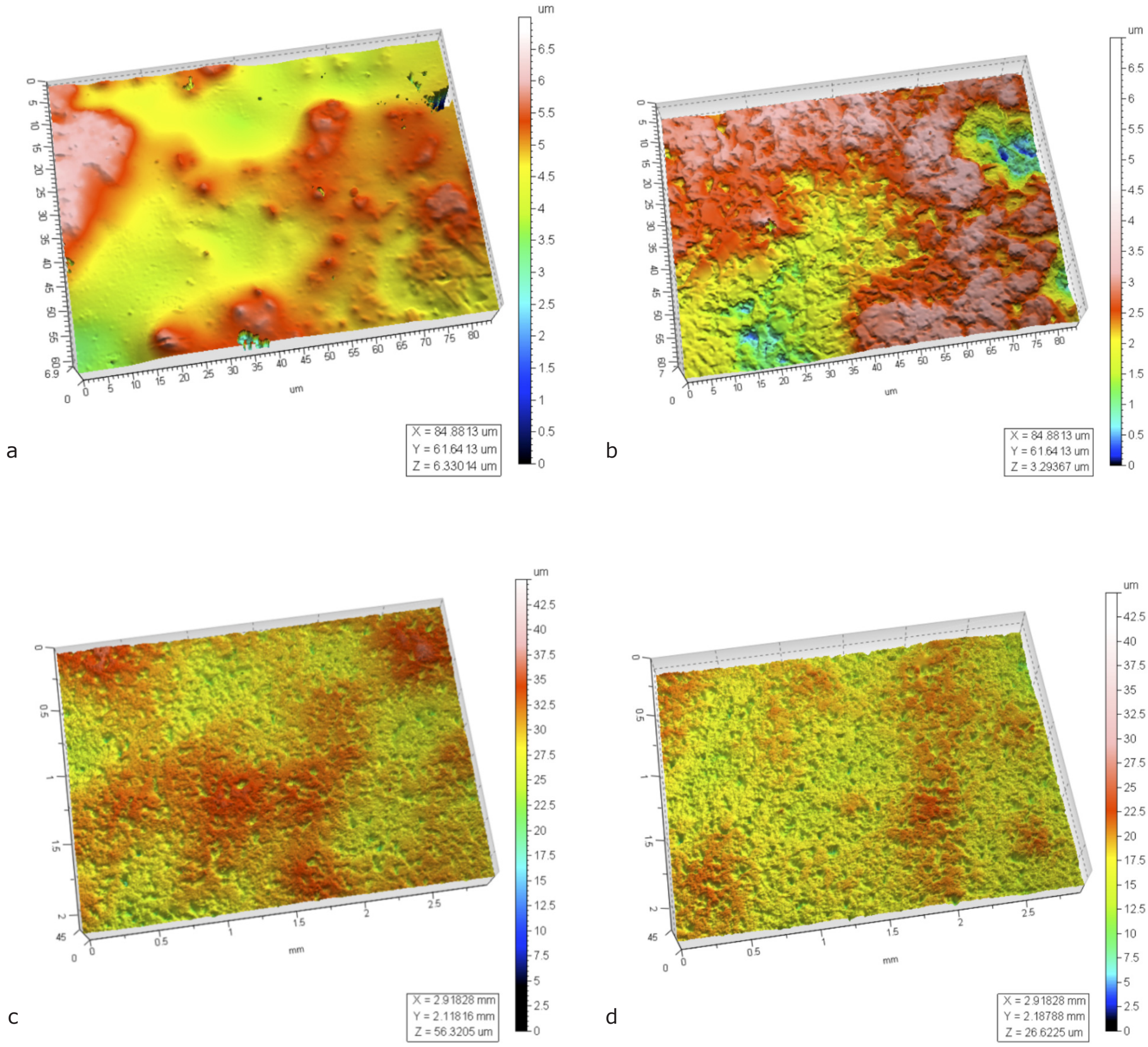

Figure 6. Confocal 3D images of sample B by using 50x objective, untreated (a) and treated (b); and by using a 10x objective, untreated (c) and treated (d).

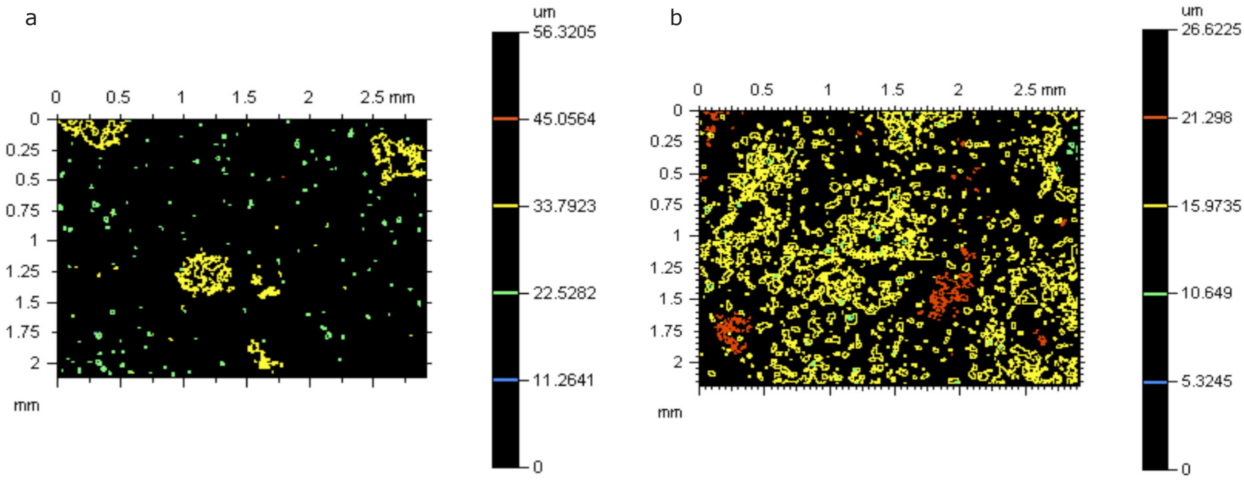

Figure 7: Contour diagrams of the confocal 3D images of sample B untreated (a) and treated (b) reported in Fig. 6 c-d, respectively.

ISO 25178 - Height parameters -		BU	BT
S_P (mm)	Maximum peak height of the Scale Limited Surface (SLS)	29.06	18.53
S_V (mm)	Maximum pit height of the SLS	27.08	19.75
S_Z (mm)	Maximum height of the SLS (sum of S_P and S_V)	56.14	38.28
S_A (mm)	Arithmetical mean height of the SLS	1.85	1.69

Table III. 3D roughness parameters of the untreated and treated sample B.

The slip resistance results determined following the standard for the ramp method for workrooms with raised slip danger (Table IV), shows that sample A, the textured one, does not improve after the treatment, maintaining the classification R9, even if the slip angle increases by 1°. Sample B, the smoother one, is not suitable for workrooms with high risk of slipping, not even after the treatment.

In barefoot areas and in wet conditions (Table V) both the samples, after treatment, AT and BT, reach the best classification, A+B+C, while the untreated samples, AU and BU, are unclassifiable.

Slip resistance, according to standard for pendulum (Table VI), is evaluated by measuring the loss of energy due to friction between rubber and the sample surface. Results show that the slip resistance is clearly improved in both the samples after the treatment.

Using the dynamometer method (Table VII), the static coefficient of friction is measured, both in dry and wet conditions. In general, values higher than 0.60 are considered good. For these kinds of samples, after treatment, the slip resistance improves especially in wet conditions.

With the Tortus method (Table VIII), the dynamic coefficient of friction is measured, both in dry and wet conditions. The Italian regulation establishes that floors in public buildings must have a friction coefficient higher than 0.40 [1]. After treatment, both the samples are suitable for this kind of intended use.

Sample	Average slip angle	Group
AU	6	R9
AT	7	R9
BU	0	UC
BT	0	UC

Table IV. Results of slip resistance with the ramp method – with footwear (DIN 51130).

Sample	Average slip angle	Group
AU	8	UC
AT	33	A+B+C
BU	11.7	UC
BT	35	A+B+C

Table V. Results of slip resistance with the ramp method – barefoot (DIN 51097).

Sample	Wet surface- PTV
AU	17
AT	25
BU	15
BT	30

Table VI. Results of slip resistance with the pendulum method in wet conditions (EN 13036-4).

Sample	Dry surface - μ	Wet surface - μ
AU	0.81	0.43
AT	0.87	0.54
BU	0.93	0.54
BT	0.98	0.63

Table VII. Results of slip resistance with the dynamometer method in dry and wet conditions (ASTM C1028).

Sample	Dry surface with leather - μ	Wet surface with rubber - μ
AU	0.37	0.42
AT	0.57	0.60
BU	0.32	0.52
BT	0.40	0.68

Table VIII. Results of slip resistance with the Tortus method in dry and wet conditions (B.C.R.).

The stain resistance (Table IX) was determined according to the international standard ISO 10545-15, by using three different staining agents and removing them from the ceramic surface after 24 hours by using different methods: hot water, weak or strong detergent, or a proper solvent. Results show that, in both the samples, the stain resistance is not compromised after the treatment, and stains are removed by flowing hot water (class 5) or by cleaning with a weak detergent (class 4).

The chemical resistance (Table X) was determined according to the international standard ISO 10545-13 by using household chemicals (ammonium chloride solution), swimming pool salts (sodium hypochloride), acid and alkalis solutions in low and in high concentrations (hydrochloric acid, citric acid, potassium hydroxide and lactic acid). After their removal, the class determination is made by visual examination. The treated samples (AT and BT) maintain the same class even if in sample BT it was not possible to perform the pencil test because the pencil lines cannot be removed by wet cloth. This is probably due to the gloss decreasing after the treatment in both the samples, but especially in sample B, caused by the chemical corrosion of the amorphous phase (Table XI)

The wettability decreases (Table XI) in both the samples after the treatment, especially in sample BT, in which the water contact angle increases by about 50° with respect to the untreated sample.

Sample	Chrome green in light oil	Iodine (alcoholic solution 13 g/l)	Olive oil
AU	4	5	4
AT	4	5	4
BU	4	5	5
BT	4	5	5

Table IX. Results of stain resistance according to the standard ISO 10545-14.

Sample	Ammonium Chloride 100 g/l Sodium Hypochloride 20 mg/l	HCL 3% V/V Citric Acid 100 g/l KOH 30 g/l	HCL 18% V/V Lactic Acid 5% V/V KOH 100 g/l
AU	GA	GLA	GHA
AT	GA	GLA	GHA
BU	GA	GLA	GHA
BT	GA(V)	GLA(V)	GHA(V)

Table X. Results of chemical resistance according to the standard ISO 10545-13 (G=glazed surface; L=low concentration of chemical agent, H=high concentration of chemical agent. Resistance classes: A=no visible effect, B=definite change in appearance, C=partial or complete loss of the original surface; (V)=pencil and reflection test not possible).

Sample	Gloss, GU	Water contact angle, Θ
AU	9.9	43.8° ± 1.5°
AT	7.3	52.2° ± 1.5°
BU	14.5	26.5° ± 1.5°
BT	9.4	77.7° ± 1.5°

Table XI. Gloss values and water contact angle of the untreated and treated samples A and B.

4. CONCLUSION

In the investigated glazed tiles, the hydrofluoric acid-based anti-slip treatment causes a chemical corrosion of the amorphous phase, while crystals (plagioclase, zircon and a-alumina) are unchanged.

Similar glazes in terms of composition but with a different surface finish, textured or smooth, give rise to quite different results, especially for the micro-roughness.

In both the glazes, the slip resistance was improved after treatment, mainly in wet conditions.

The maintenance of performances after treatment was verified in both the samples, even if a decrease of gloss (about 30%) was detected.

REFERENCES

[1] Indagini statistiche sull'industria italiana delle piastrelle di ceramica, 33a edizione, anno 2012, Confindustria Ceramica.

[2] F. Quirion, A. Massicotte, S. Boudrias, P. Poirier, The impact of a chemical treatments on wear, gloss, roughness, maintenance and slipperiness of glazed ceramic tiles, Journal of Environmental Health Research, 9 (2), 97-110, 2009.

[3] F. Quirion, P. Poirier, Surface properties and slip resistance of glazed ceramic tiles over-treated, or treated multiple times, with hydrofluoric acid, Journal of Environmental Health -Research, 11 (1), 17-27, 2011.

[4] A. Escardino, J.L. Amorós, A. Gozalbo, M.J. Ortis, F. Lucas, A. Belda, Interacción entre capas de esmalte durante la cocción de los vidriados resultantes, 201-217, Qualicer 2002.

[5] L. Fröberg, L. Hupa, M. Hupa, Corrosion of the crystalline phases of matte glaze in aqueous solutions, journal of the European Ceramic Society, 29, 7-14, 2009.

[6] L. Fröberg, T. Kronberg, S. Tornblom, L. Hupa, Chemical durability of glazed surfaces, Journal of the European Ceramic Society, 27, 1811-1816, 2007.

[7] L. Esposito, E. Rambaldi, A. Tucci, G. Bonvicini, A. Albertazzi, G. Timellini, Chemical ageing and microstructural changes of glazed ceramic tile surfaces, cfi/Ber. DKG, 85 (6), 64-67, 2008.

[8] V. Cannillo, L. Esposito, E. Rambaldi, A. Sola, A. Tucci, Microstructural and mechanical changes by chemical ageing of glazed ceramic surfaces, Journal of the European Ceramic Society, 29, 1561-1569, 2009.

[9] E. Bernardo, L. Esposito, E. Rambaldi, A. Tucci, Recycle of waste glass into "Glass-ceramic stoneware", Journal of the America Ceramic Society, 91 (7), 2156-2162, 2008.

[10] R.A. Eppler, D.R. Eppler, Glazes and glass coatings, Chemical durability, 253-270, The American Ceramic Society Ed., 1998.

[11] Italian regulation, D.M. n° 236-6/89, 14/06/1989.