ANALYTICAL INVESTIGATION ON ACID AND ALKALINE ATTACK ON GLAZED TILE SURFACES

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ABSTRACT

With a view to achieving a better understanding of the attack action of ISO 10545.13 standard solutions (HCl 18 % w/w and KOH 100 g l^{-1}) on the glazed surfaces of ceramic tiles, samples of "Porcelain Stoneware" tiles were prepared in the laboratory or obtained by industrial production.

Glazed, fired surfaces, containing known glazes and pigments were characterized by X Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM), after which chemical attack tests were run.

The leaching solutions obtained were analyzed by ICP-aes spectroscopy, and by comparison of the leaching solutions obtained from pure pigments, and the attacked surfaces were, again, observed by SEM and AFM and their structure verified by XRD.

It was, thus, possible to verify the very scarce alkaline attack on the glaze components, while reaction in HCl led to a selective solubility of the Al– and Alkali-based components, sometimes also together with pigment solubilization.

Moreover, interesting results were obtained by firing the same ceramic tiles samples with the same cycle to different maximum temperatures, verifying the differences in chemical attack resistance, and testing in the same ways similar industrially produced tiles, with different glazes.

1. INTRODUCTION

Ceramic tiles are considered valuable with respect to other possible flooring and walling materials because of their attractive surface appearance, cleanability, easiness of hygienic care, and their stability and resistance to loads, abrasion, stains etc. Among these latter features, resistance to chemical attack is considered one of the more relevant qualities, so that a set of standard tests has been established to enable simulating the behaviour of ceramic surfaces, glazed or not, under very heavy attack conditions, such as by pure acid or alkaline chemicals, or under lighter attack, such as that provided by solutions simulating commonly employed cleaning products. The foregoing is all set out in the ISO 10545.13 standard, which substitutes EN 106 and EN 122.

In any event, these attacks are evaluated by a "standard" observation, which may be with the help of pencil marks, but always in a qualitative way.

It was considered it could be very interesting, however, to study how these attack occur, and how they really modify the ceramic surface, inducing the solubilization of some less resistant chemical or mineral ceramic compound, present on the surfaces, by the analytical control of leached solutions, in order to understand, too, how to design new glazes and new surfaces, able to increase their performance under chemical attack.

2. EXPERIMENTAL

The experimental work was organized as follows:

- Selection of glazed industrially produced tiles, with low (< 0.3 %) water absorption, sensitive to maximum temperature variation, to enable performing different firing tests
- Selection of the main pigments, utilized for the production of tested glazes
- Chemical attack tests, both on glaze surfaces and on pigment powders, by ISO 10545.13 standard procedure, testing different chemical solutions containers and materials, to permit the recovery of pure leaching solutions
- Analytical characterization, before and after the attack, of the surfaces, by SEM-EDS and AFM microscopy , by XRD, X ray diffraction and by Visible Spectroscopy, through Colorimetry
- Quantitative chemical analysis of leaching solutions by ICP atomic emission spectroscopy
- Same procedures, but on differently fired samples (different maximum temperature and/or different firing cycle), to verify their influence on chemical attack

2.1. SELECTED TILES AND PIGMENTS

Industrially produced tiles (cm. 30 x 30) were mainly glazed by lattice-modifier rich glaze [A], but three more glazes were tested, being a fluxing, Lead and Boron-based one [B] containing Zr to stabilize itself, a matt glaze at high content of Zn, Zr and Sn [C], and, finally, a "metal-finish" glaze, having high content of Phosphorus and Iron oxides and known to have scant resistance to acid attack .

Glaze compositions are summarized in Table 1.

To better understand the role of pigments in the resistance to chemicals (is it the glaze solubilizing into the acid or alkaline solution, bringing in solution also the pigments, or it is the pigment itself being leached by the attack solution ?), two main, well known pigments were utilized for the experiments: a blue one, a Spinel composed of Cobalt Aluminate , having a very strong lattice, and a pink one, Zircon structure composed by Zr – Si – Fe, considered to be a solid solution of Iron in Zirconium Silicate, or the inclusion by sintering of a Hematite molecule in a crystalline lattice of Zircon.

Both pigments were added to the glazes at 3 % w/w.

Particularly glaze [A] was, then, tested for its reaction with firing temperature variation: tiles were fired by a 45 minutes cycle, cold to cold, till 1190, 1200, 1210 and 1230°C, while pigmented glaze was fired at 1140, 1170, 1200 and 1210°C . It was easy to note, just by an observation of the tile surface, that pink Zircon glazes assumes lighter colours with the increase of the firing temperature, while blue Spinel glazes becomes darker with the increase of temperature.

Water absorption of fired tiles, verified by ISO 10545.3, gave values decreasing from 0.36 % at 1190°C, to 0.04 % at 1210°C and increasing again if fired at 1230°C to 0.33 %.

	GLAZE A	GLAZE B	GLAZE C	GLAZE D
CaO	8.96	4.25	6.12	7.11
MgO	3.42	0.06	0.15	1.02
K_2O	3.07	0.76	1.95	2.43
Na_2O	5.63	0.53	0.94	2.10
Al_2O_3	25.28	4.88	7.56	12.12
Fe_2O_3	0.08	0.09	0.11	19.18
TiO_2	0.03	0.03	0.03	-
SiO_2	53.52	34.05	44.81	32.24
PbO	-	31.44	1.06	-
ZnO	-	4.92	6.12	-
B_2O_3	-	9.06	3.48	-
SnO_2	-	-	10.04	-
WO_3	-	-	4.01	-
ZrO_2	-	5.88	12.86	-
P_2O_5	-	-	-	24.04
BaO	-	0.01	1.39	-
Li_2O	-	0.21	-	-

Table 1. Composition of glazes

2.2. CHEMICAL ATTACK TESTS

Both, acid and alkaline attack, were made following the ISO 10545.13 standard method, thus utilizing HCl 18 % w/w (Erba Analytics RP 37 % w/w) and KOH 100 g l^{-1} (Erba Analytics RP > 85 %, less than 0.0001 % of impurities) with bi-distilled water, in Teflon™ containers, to avoid any contamination from the vessels. Leaching time was, as stated, 4 days at laboratory conditions (21 – 24°C).

Particular care was given to the choice of reaction tubes and of sealing materials: in order to analyze the reacted solutions, it was necessary to avoid any leaching from those materials, to evaluate the real release from tiles. In fact, for instance, the foreseen use of common boron-silicate glass is inapplicable, as by alkaline attack a sure solubilization of Boron will occur. After many different attempts with various materials, best results were obtained (and tested by leaching tests and subsequent ICP analyses) by Pyrex™ glass tubes, ∅ mm. 23, cut cm. 10 high.

The first care on applying the sealant was to avoid putting it also on the surface inside the glass tube, to be sure that the attack solutions will operate always on the same glaze surface. Sealant material, again, had to be tested for its release in acidic and alkaline media: no Silicone polymers, nor Styrene ones, Butyl one, Acrylates, Paraffin waxes etc. gave good effects in both media. The final choice was to use transparent Silicone for the acid attack (very good adhesion and no leaching, but poor adhesion in alkaline media) and Plasticine (mix of aliphatic waxes) for the alkaline attack (these waxes disperse many Ca ions in acid media).

2.3. SEM-EDS

Electronic Microscope images were obtained by Philips XSEM instrument, 25 KeV, spot 5, WD av. 10.5 mm. on samples surfaces after ion sputtering deposition of av. 8 nm of Au; EDS microanalyses were got by Oxford INCA system.

2.4. AFM

Atomic Force Microscopy was executed on some selected samples by a Park Scientific Instrument, both, by constant high and constant strength, on approx. μm 50 x 50 areas.

2.5. XRD

Mineralogical, crystallographic analyses were obtained on real surfaces by PANalytical X'PERT PRO instrument, utilizing as incident radiation Cu K_{α}, Ni filter, at 40 kV and 40 mA, with an X'Celerator detector. The analyzed surface can be estimated by a collimation of cm. 0.8 x 1.5, in a 2 ϑ range from 5 to 65.

2.6. COLORIMETRY

By an UV-Vis. Spectroscopy, Minolta CM-2600d, diaphragm of 8 mm, lighting D65 at 2° angle, utilizing HUNTERLab system, colorimetric analyses of surfaces before and after the chemical attack were obtained, to evaluate colour changing.

2.7. CHEMICAL ANALYSIS

Quantitative chemical analysis was made on leaching solutions, utilizing Atomic Emission Spectroscopy, through a Perkin Elmer Optima 4200 DV instrument, giving simultaneously the spectra of all the emissions of all the present elements. Acidic leaching solutions were analyzed as they were, while the alkaline ones, to prevent precipitation and corrosion of Quartz items, had to be diluted and buffered. Of course, major interpretation problems were found for Na, K and Ca, which are easily ionized, often giving saturation of the signal on the detector. As already cited, blank analyses were always made to assure that the system was not influencing the leaching result.

3. RESULTS AND DISCUSSION

The results hereafter reported refer mainly to Glaze [A] application, as it was considered the most utilized in the production of such industrial tiles; moreover, AFM and colorimetric results and other glazes analyses will be object of a further publication.

The comparison of XRD analysis of untreated and leached surfaces was not useful to understand the behaviour of the attack: in Figure 1, as an example of the most obtained, is possible to see how the appearance of XRD for glaze [A] is very similar before and after any treatment.

In Figure 2 are reported and compared the XRD of blue and pink pigmented glazes, before any attack: it is possible to appreciate that while the diffractogram of the blue sample is quite identical to the one of the not pigmented surface (so, the pigment was completely absorbed by the glassy phases of glaze), the pink coloured glaze still brings signals of the pigment, like the ones due to Zircon at 20.046, 27.022, 33.781 and 35.680 ° 2ϑ.

The comparison of XRD obtained from the same surface of pigmented glaze, before and after the chemical attack, on the contrary, do not reveal any major difference, letting to suppose that the attack is effective on the amorphous glassy phases, and not directly on the pigment structure (Figure 3).

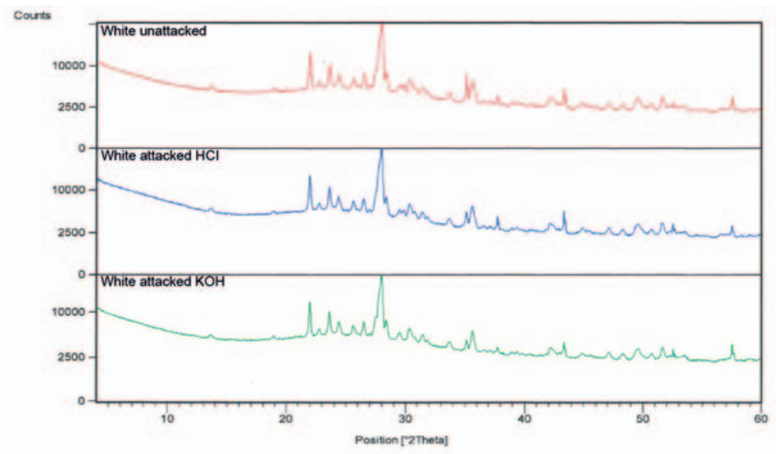


Figure 1. XRD comparison of unattacked (top), acid attacked (centre) and Alkali attacked (bottom) surfaces

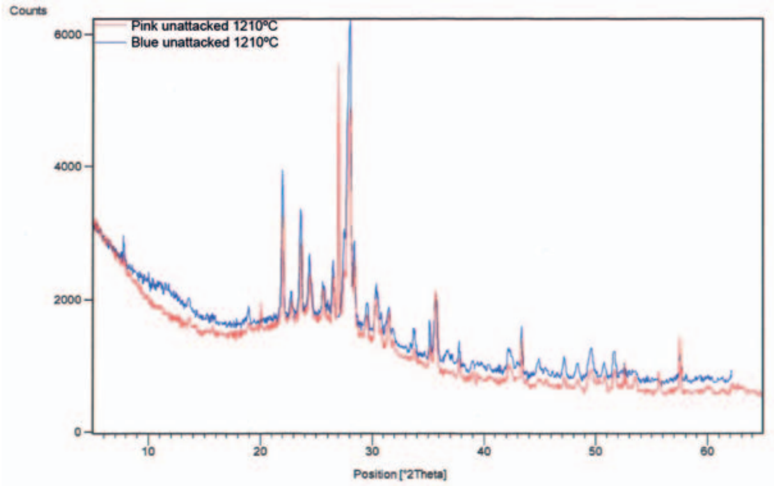


Figure 2. XRD comparison of unattacked surfaces, blue (top) and pink (bottom) pigmented

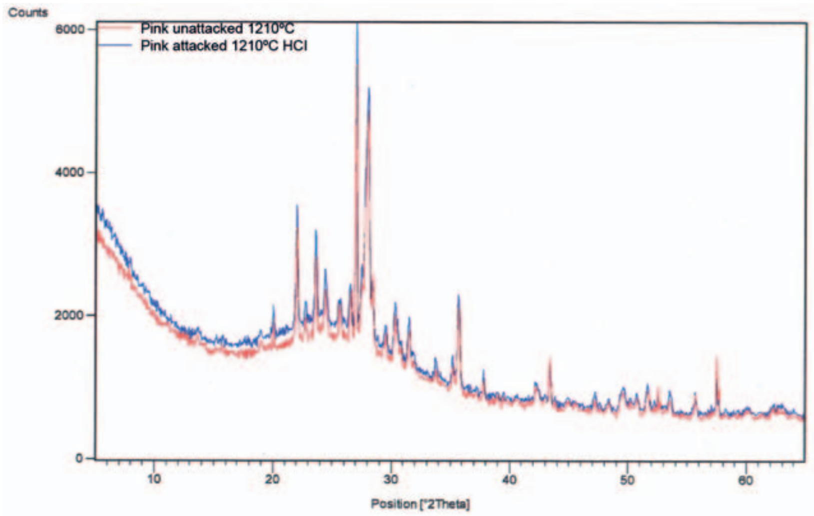
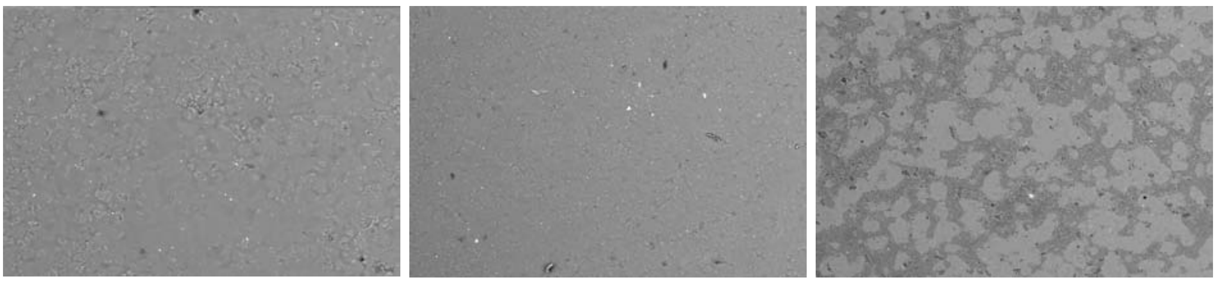


Figure 3. XRD comparison of pink pigmented glaze before (top) and after (bottom) the chemical attack

Very interesting was the analysis of surfaces by **SEM**: main observations were made at 100X and 200X magnification, increasing it till 2000X where some interesting particulars were noticed. Here are reported the results obtained on glaze [A] samples, which represent well the general behaviour. On not pigmented glaze samples, for instance fired at 1190°C, nearly to maturation temperature, it is very clear that alkaline attack is not effective on any glaze phase, while acid attack is very active on destroying the non-glassy phases. Figure 4 reports a comparison of Secondary Electron images taken at 100X.



[1] Not attacked *[2] Attacked by KOH* *[3] Attacked by HCl*

Figure 4. 100X SEM images on unpigmented glaze [A] surface, fired at 1190°C

While on surface [1] the glassy surfaces (smooth) and the crystalline ones (rough) have the same composition, based on Silicon-aluminates of Ca, Na, K, Mg and Na, an enlargement to 1600X of the acid attacked one [3], shows that intergranular cracks are present after attack and that the remaining smooth areas are composed practically by amorphous Silica.

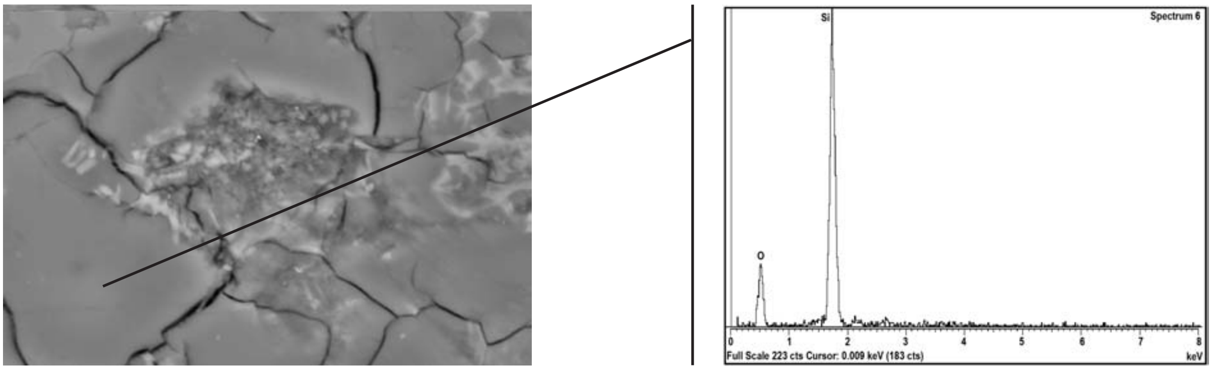


Figure 5. Acid attacked surface, 1600X, with EDS microanalysis of smooth areas = amorphous Silica

Glaze [A] + blue pigment gave exactly the same results like unattacked one, and did not show any action by KOH, while HCl leached the surface of fired tile, leaving amorphous silica areas, like shown in Figures 4 and 5. Very slight evidence of Co presence in microanalysis disappeared after acid attack and was still present after alkaline attack, but, anyway, SEM-EDS analyses are not sensitive enough for any significant chemical analysis.

Glaze [A] + pink pigment, both, on not attacked and HCl or KOH attacked samples, show the presence of the alkaline and alkaline-earth alumino-silicate matrix, and the presence of diffused Zircon rich areas, that persist also after attack (Figure 6)

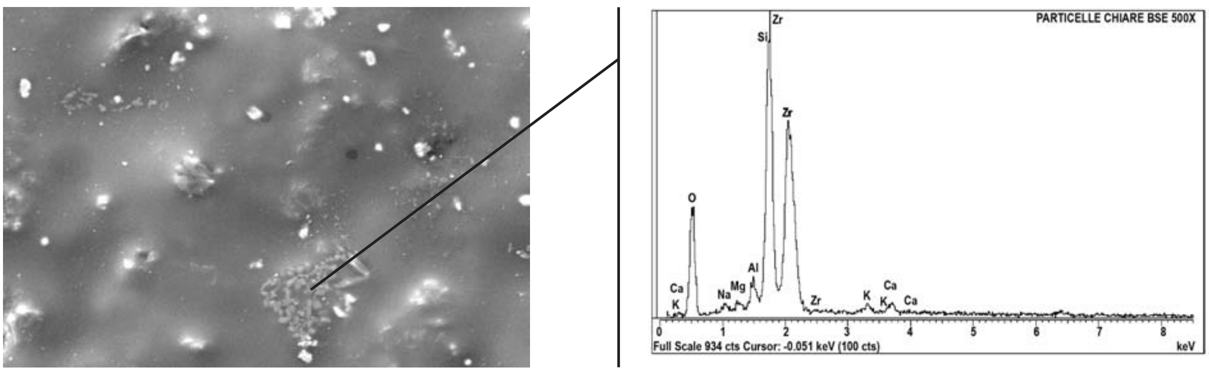


Figure 6. Pink pigmented glaze [A], with Zircon crystallization (1000X), not attacked

ICP chemical analysis on leached solutions, finally, gave the following results, confirming the efficiency of acid attack respect with the alkaline one:

HCl attack	At 1190°C	At 1200°C	At 1210 °C	At 1230 °C
Ca	38.5 ± 0.3	22.1 ± 0.2	20.1 ± 0.2	94 ± 1
K	17.8 ± 0.3	8.4 ± 0.2	8.0 ± 0.3	47 ± 3
Mg	12.8 ± 0.3	6.6 ± 0.1	6.3 ± 0.1	34.7 ± 0.4
Na	30.1 ± 0.4	14.4 ± 0.4	13.2 ± 0.5	74.4 ± 0.6
Al	80 ± 1	44.6 ± 0.3	39.3 ± 0.3	180 ± 2
Fe	541 ± 2	314 ± 4	293 ± 3	1.4 ± 0.1
Ti	50 ± 2 ppb	34 ± 1 ppb	30 ± 1 ppb	95 ± 1 ppb
KOH attack	**At 1190°C**	**At 1200°C**	**At 1210°C**	**At 1230 °C**
Ca	8.2 ± 0.7	6.4 ± 0.6	6.8 ± 0.4	7.6 ± 0.3
Mg	1.6 ± 0.3	780 ± 12 ppb	1.4 ± 0.2	1.2 ± 0.1
Na	9.6 ± 0.5	10.3 ± 0.8	8.7 ± 0.2	12.0 ± 0.6
Al	10.7 ± 0.8	5.8 ± 0.3	3.6 ± 0.4	16.3 ± 0.6
Fe	486 ± 9 ppb	170 ± 6 ppb	340 ± 5 ppb	274 ± 8 ppb
Ti	Tr. = < 0.01 ppm	Tr.	Tr.	12 ± 2 ppb

Table 2. Release of elements, verified by ICP, on glaze [A], not pigmented

HCl attack	Co 1140°C	Co 1170°C	Co 1200°C	Co 1210°C
Ca	52.4 ± 0.2	28.2 ± 0.3	15.3 ± 0.2	8.4 ± 0.3
K	42 ± 2	19.3 ± 0.4	10.4 ± 0.4	8.9 ± 0.5
Mg	27.3 ± 0.5	12.8 ± 0.2	10.4 ± 0.3	7.8 ± 0.2
Na	55 ± 2	30.6 ± 0.6	14.8 ± 0.2	12.1 ± 0.3
Al	104 ± 3	62 ± 2	40 ± 1	28.2 ± 0.4
Fe	850 ± 8 ppb	485 ± 6 ppb	386 ± 5 ppb	304 ± 6 ppb
Ti	Tr.	Tr.	Tr.	Tr.
Co	8.3 ± 0.2	4.1 ± 0.2	3.4 ± 0.3	2.8 ± 0.1
KOH attack	**Co 1140°C**	**Co 1170°C**	**Co 1200°C**	**Co 1210°C**
Ca	10.3 ± 0.4	8.9 ± 0.2	9.6 ± 0.3	6.8 ± 0.2
Mg	2.8 ± 0.1	5.4 ± 0.2	4.6 ± 0.1	3.6 ± 0.1
Na	10.6 ± 0.4	12.8 ± 0.4	10.1 ± 0.3	6.6 ± 0.2
Al	15.4 ± 0.3	10.6 ± 0.2	8.5 ± 0.1	6.3 ± 0.1
Fe	Tr.	28 ± 1 ppb	Tr.	36 ± 2 ppb
Ti	Tr.	Tr.	Tr.	Tr.
Co	240 ± 13 ppb	210 ± 7 ppb	264 ± 9 ppb	197 ± 11 ppb

Table 3. Release of elements, verified by ICP, on glaze [A], pigmented by blue Spinel

To better understand the behaviour of pigmented surfaces, the chemical attack test was executed also on single pigments, as powders like they are used to be added to the glazes, with the following results:

Pigment	Co	Zr	Al	Fe	Ca	K	Na	Mg
Blue	8.7 ±0.2	--	42.5± 0.4	430 ppb	29.5 ±0.4	2.2 ± 0.3	10.0± 0.4	6.6 ± 0.2
Pink	--	2.2 ± 0.1	1.3 ± 0.1	22.6± 0.3	8.1 ± 0.4	2.6 ± 0.3	2.0 ± 0.3	38.5± 0.4

Table 4. Release of elements, by HCl attack, from single pigments

HCl attack	Zr 1140°C	Zr 1170°C	Zr 1200°C	Zr 1210°C
Ca	16.0 ± 0.2	16.5 ± 0.3	12.5 ± 0.3	6.4 ± 0.2
K	7.6 ± 0.3	8.4 ± 0.6	6.4 ± 0.5	4.6 ± 0.3
Mg	5.9 ± 0.4	5.4 ± 0.3	4.1 ± 0.2	3.5 ± 0.3
Na	12.3 ± 0.7	15.5 ± 0.6	10.1 ± 0.3	6.6 ± 0.3
Al	29.6 ± 0.4	35.6 ± 0,6	28.4 ± 0.8	18.3 ± 0.4
Fe	1.5 ± 0.1	1.1 ± 0.1	706 ± 12	518 ± 12
Ti	Tr.	Tr.	Tr.	Tr.
Zr	130 ± 4 ppb	156 ± 6 ppb	114 ± 7 ppb	64 ± 5 ppb
KOH attack	**Zr 1140°C**	**Zr 1170°C**	**Zr 1200°C**	**Zr 1210°C**
Ca	8.0 ± 0.3	9.5 ± 0.5	6.7 ± 0.4	4.8 ± 0.5
Mg	3.7 ± 0.3	2.3 ± 0.2	1.4 ± 0.2	1.1 ± 0.1
Na	4.2 ± 0.3	5.0 ± 0.2	6.3 ± 0.5	7.2 ± 0.3
Al	8.6 ± 0.2	12.4 ± 0.3	7.5 ± 0.4	6.1 ± 0.2
Fe	286 ± 12 ppb	356 ± 8 ppb	312 ± 12 ppb	258 ± 7 ppb
Ti	Tr.	Tr.	Tr.	Tr.
Zr	Tr.	Tr.	Tr.	Tr.

Table 5. Release of elements, verified by ICP, on glaze [A], pigmented by pink Spinel

4. CONCLUSIONS

As it was foreseeable, the large amount of alkaline and alkaline-earth oxides, of not acidic nature, contained by the fired glaze surface, even if Silica amounts are present, make these layers more exposed to acid attack and less sensitive to the alkaline one. The effect of firing temperature is of scarce importance till the glaze is fully matured and in sintering-melt conditions (in these experiments, till 1210°C), while a further increase of temperature, according to the sudden multiplication of porosity due to micro bubbles and the weakening of glass lattice, let the aggression by chemicals to be more and more effective.

Generally, the amount of leached cations is to be considered proportional to the amount of element contained by the surface, following the trend Al > Ca > Na > other elements. Chromophore elements have always low losses.

Practically, the acid attack by HCl 18 % w/w extracts from the glassy matrix all the cations, leaving only amorphous Silica. This could be due to the relevant charge/ radius rate of Cl^- ion, which permits a very stable bonding with alkaline and alkaline-earth cations and with Aluminium, too, weakening the existent bonds with Oxygen, present in the glass lattice. Aluminium, moreover, even if it is a lattice stabilizer, being an amphoteric element, is the only one revealing a quite high reactivity with KOH.

If the pigments are present, the leaching behaviour does not significantly change.

Co leaching from blue Spinel is really relevant, with respect to its very low amount in the pigment, as this pigment is completely removed by HCl, together with the glassy phases into which it is melted.

Zr leaching from pink Zircon, on the contrary, is very scanty, due to the resistance of Zircon crystalline "islands", like observed by SEM.

Some of these conclusions can be appreciated by the following figures:

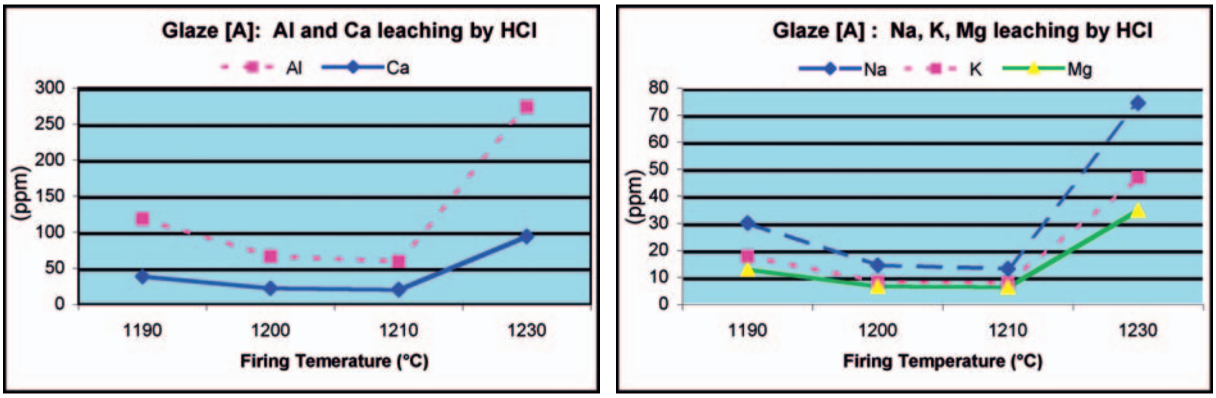


Figure 7. Cation leached by HCl vs. firing temperature of Glaze [A]

By a general observation of data obtained by chemical analysis it is, also, possible to note that glazes with pigment release, at the same temperature conditions, less cations in solution, not only in pink glazes, where the presence of Zr decreases, as seen, the possibility to attack the surface, but also when blue glaze is tested, even if it is more sensitive to chemicals.

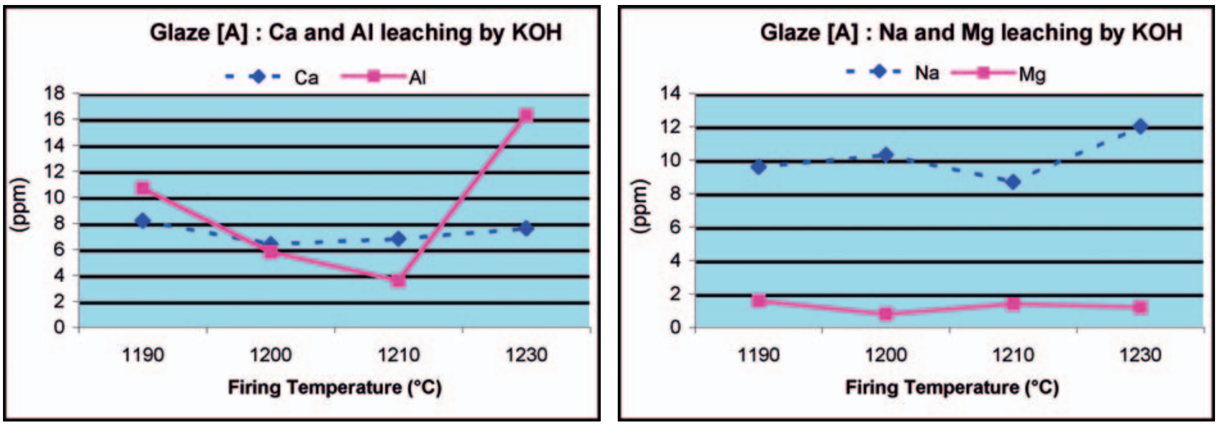


Figure 8. Cation leached by KOH vs. firing temperature of Glaze [A]

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