INTERACTION BETWEEN GLAZE LAYERS DURING FIRING. CHEMICAL RESISTANCE OF THE RESULTING GLAZES

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ABSTRACT

Ceramic tile glazes are obtained by applying frits, frit blends or frits with crystalline aggregates, as aqueous suspensions, organic suspensions (screen printing) or by dry application in granular form on a base glaze layer, followed by firing. During firing the components of the applied layers can give rise to liquid phases (melts) and crystalline phases of different nature, which can interact with each other by diffusion of their components. The degree of diffusion depends on the composition of the raw materials, melt viscosity and the thermal cycle used in firing. The present study addresses the effect of the interaction between the phases making up this layer of heterogeneous composition, on the resistance to chemical attack of the resulting glazes.

1 INTRODUCTION

Ceramic tiles are subjected during use to contact with cleaning agents that sometimes contain aggressive chemical products. Glazed tile behaviour on exposure to chemical attack is determined by the characteristics of the glaze coating, and is evaluated by direct tests on the finished product according to standard methods, which consist of depositing certain chemical reagents on the glazed surface[1]. The result of these tests provides empirical information on glaze behaviour, but it does not allow predicting how modification of the glaze composition will affect fired glaze resistance to chemical attack.

In silicate glasses, acid attack takes place by hydronium ions that extract modifying ions from the network[2,3], leaving an external layer of silica gel in which the alkaline and alkaline-earth cations have been leached. As a result of leaching, this layer shrinks producing cracking and sometimes peeling of the surface [4]. If attack takes place by an organic acid with a chelating effect (citric, lactic, oxalic acid, etc.), it can be more aggressive because soluble complexes are formed with some of the extracted cations, increasing the leaching rate [4,5,6]. Alkaline attack leads to dissolution of the SiO_2 network by rupture of the Si-O-Si bonds[7].

The effect of the various oxide components on glass chemical resistance has been widely studied [2,8,9]. Silica glass is generally quite resistant to acid attack but resistance decreases on incorporating network modifiers, increasing the tendency to leach as the silica content decreases [4]. The different glass attack mechanisms depending on the pH of the solution in contact with the glass indicate that glasses with a high modifier content will be resistant to network dissolving processes ($pH>9$), and that glasses with a high network former content will be resistant to dealkalinization processes [10].

The drop in resistance to acid attack caused by network modifiers becomes greater as their field intensity decreases. Replacing alkalis by alkaline earths generally leads to more resistant glasses, and the literature reports the stabilising effect of calcium and zinc on the vitreous network in some systems [11,12]. The rise in Al_2O_3 and B_2O_3 content increases glass resistance to dealkalinization, until certain quantities are reached, beyond which the glasses become more attackable by acids [10,8,13]. Adding ZrO_2 raises the chemical resistance of silicate glasses [9,14,15].

Ceramic glazes present a greater diversity than glasses, and can range from homogeneous glasses to materials made up of several crystalline phases embedded in a glassy matrix, in which immiscible liquid-phase separation can also occur. Chemical attack on a ceramic glaze can act on any of its components, and in principle, many of the results found for glasses are applicable. It is necessary to consider that in most glazes, chemical attack is not uniform because glaze microstructure is not homogeneous, and that this microstructure can alter (changing the nature and proportion of the crystalline or glassy phases, and hence residual glass composition) on modifying thermal treatment or particle size of the components, or if the different materials contained in the glaze react with each other.

2 EXPERIMENTAL

Four glaze suspensions were prepared as bases (B1 to B4), together with three screen printing inks (S1 to S3), two glaze suspensions for bell application (C1 and C2) and two frits in granular form (G1 and G2). Table 1 details the glassy and crystalline components that make up each of these materials.

Mixture	Glassy components	Crystalline components
B1	opaque zirconium frit and transparent frit	kaolin, quartz, zircon, corundum
B2	transparent frit	kaolin, quartz, zircon, corundum
B3	opaque zirconium frit	kaolin, quartz, zircon, corundum
B4	matt barium frit	feldspar, quartz, zircon, corundum
S1	matt barium and zinc frit	wollastonite, quartz, kaolin
S2	opaque zirconium frit	kaolin, zircon
S3	matt barium frit	kaolin
C1	matt barium frit	wollastonite, feldspar, kaolin
C2	transparent frit	wollastonite, feldspar, kaolin
G1	zirconium and calcium frit	-
G2	matt barium frit	-

Table 1. Components of the mixtures used to make the glazes.

The base glazes were applied by a bell on green floor tile bodies. The corresponding applications were subsequently performed on these bases of the screen printing inks, glaze suspensions and a 50% mixture of granulars G1 and G2. The resulting pieces were fired in an industrial kiln with a thermal cycle similar to those used for white-firing floor tiles, with a peak temperature between 1160 and 1170°C. The surface of the glaze produced by application of G1 and G2 was polished in a laboratory facility.

Glaze resistance to attack by concentrated HCl and lactic acid was determined according to the method described in the standard [1]. Glaze microstructure was observed with a scanning electron microscope (SEM) fitted with an energy-dispersive X-ray analysis instrument.

3. RESULTS

3.1 GLAZES PRODUCED WITH THE BASE GLAZES

Table 2 details the results of acid attack on the glazes made with bases B1 to B4.

	B1	B2	B3	B4
Lactic acid 5%	GHA	GHB	GHA	GHA
HCl 18%	GHA	GHB	GHA	GHB

Table 2.

Glaze B1 (Figure 1) contains zircon (clear particles in the photograph), corundum, kaolin and quartz as crystalline components. The glassy raw materials are a mixture of a transparent and a white zirconium frit. The resulting glaze is not attacked due to the high silica content of the transparent frit, which is strengthened by the partial dissolution of the quartz, and by the presence of zircon in the glassy phase.

Base B2 is made with a transparent frit, which is in principle not very attackable, with quartz, and zircon and corundum additions. This base has a greater proportion of glassy phase than B1 (Figure 2).

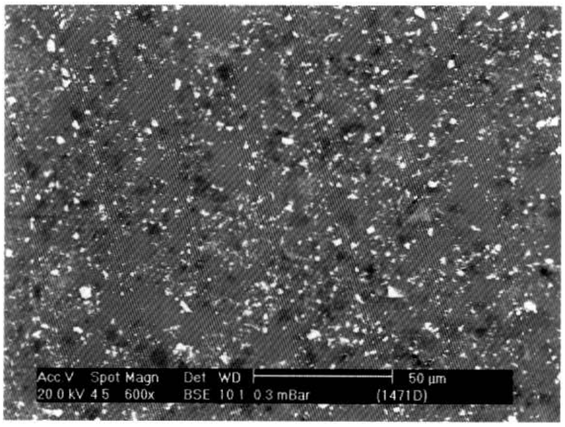

Figure 1. Surface of the glaze made with B1.

Due to its characteristics, the resulting glaze should not be attacked, but a GHB classification is found. On observing the surface of the glaze treated with HCl (Figure 3) and with lactic acid, it can be appreciated that the attack has occurred around the added corundum (porous agglomerates of very fine particles), either on the corundum itself or on the glass resulting from its reaction with the melt. According to the literature [8,13], alumina increases glass chemical resistance except in very high proportions, in which case a change takes place in the co-ordination of this oxide, yielding an attackable glass.

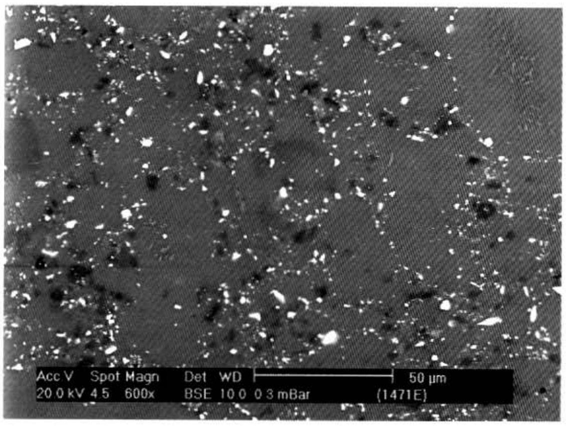

Figure 2. Surface of base B2..

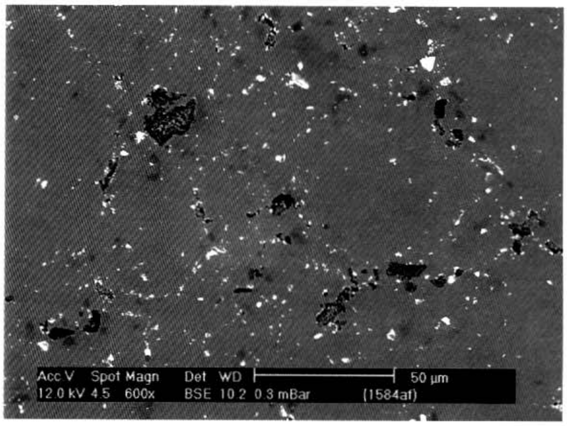

Figure 3. Surface of base B2 etched with HCl..

Base B3 contains an opaque zirconium frit with quartz, zircon and corundum additions, the last two of very fine particle size. In the resulting glaze (Figure 4) these crystalline phases are observed together with the acicular zircon crystals that devitrified from the frit. This glaze is not attackable, just like B1.

Base B4 is made from a matt barium frit without added crystalline materials. The surface of the resulting glaze is completely covered with barium aluminosilicate crystals, forming a rough texture with very little glassy phase, in which certain open pores remain because bulk crystallisation has arrested sintering (Figure 5)[16].

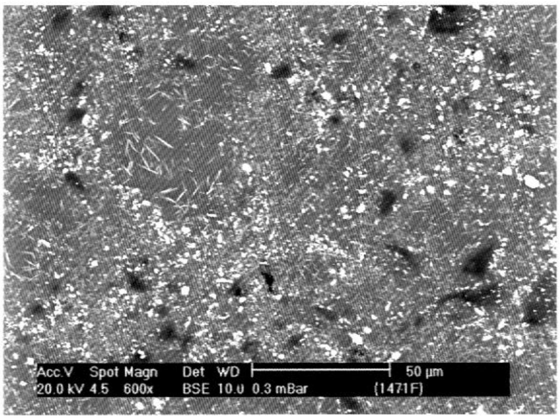

Figure 4. Surface appearance of the glaze made with base B3.

The attack it undergoes with hydrochloric acid is relatively slight, as Figure 6 shows, and seems to occur on the glassy phase. Lactic acid does not alter glaze microstructure.

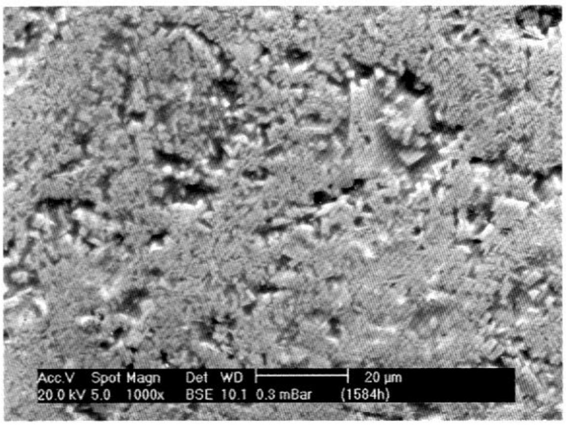

Figure 5. Surface of the glaze made with base B4.

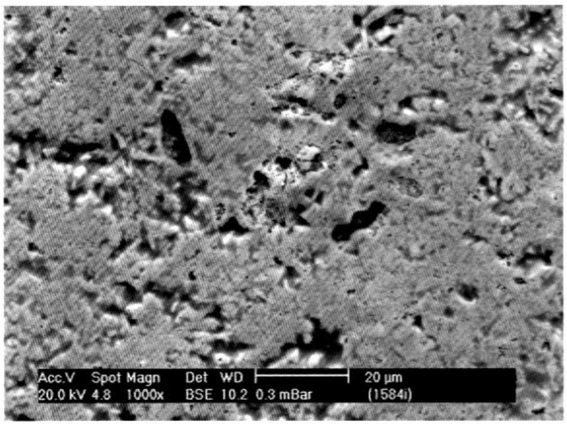

Figure 6. Surface of base B4 etched with HCl.

3.2 GLAZES PRODUCED BY SCREEN PRINTING.

3.2.1 Effect of screen printing on the attackability of the resulting glazes.

To analyse the influence of the screen printing application on the resistance to acid attack of the resulting glazes, B4 was selected out of the previous bases, since it was compositionally closest to the industrial barium matts and presented a moderate resistance to acid attack. The three screen printings described in section 2 were applied to this base. Table 3 details the test results of their resistance to hydrochloric and lactic acid attack.

Base	Screen printing	18% HCl	5% lactic acid
B4	S1	GHB	GHB
	S2	GHA	GHA
	S3	GHB	GHA

Table 3. Results of the acid resistance test.

Screen print S1 consists of a mixture of a matt barium and zinc frit with wollastonite, quartz and kaolin. The glaze produced by application to B4 (Figure 7) contains crystallised barium aluminosilicates and anorthite, this last material resulting from the reaction of kaolin with the calcium in the glassy phase. On the surface of the etched glaze (Figure 8), it can be observed that attack has taken place on the glassy phase with both acids, leaching the modifier cations and leaving a crazed silica gel skeleton [2].

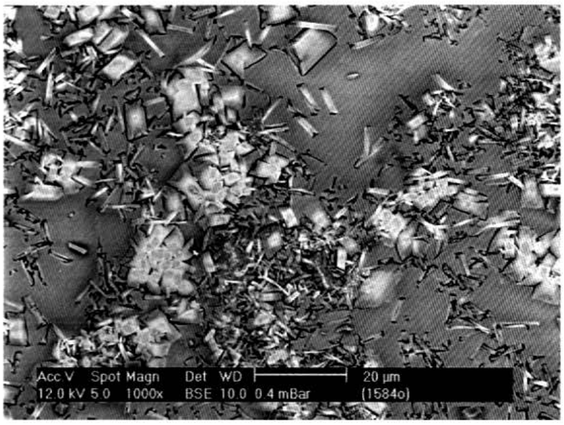

Figure 7. Surface of glaze S1B4.

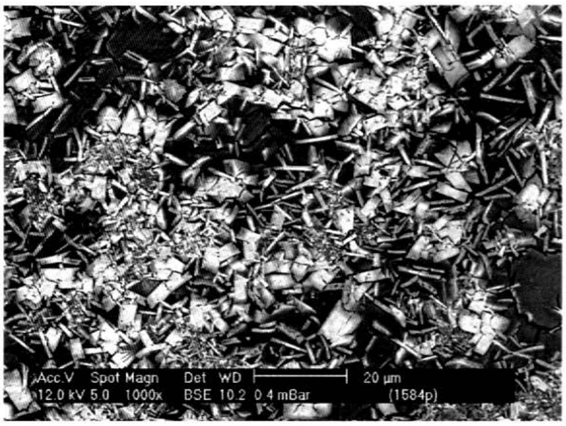

Figure 8. Surface of S1B4 etched with 18% HCl.

The cross section of the etched glaze (Figure 9) shows that attack has not only taken place on the uppermost layer, but has surprisingly leached the glassy matrix to a thickness of 40 to 50 μm, while the crystals and initially added kaolin remain. On comparing this with the cross section of the original glaze (Figure 10), it can be observed that the attack affects the whole thickness of the screen print, stopping at the base, with which no interaction seems to have occurred.

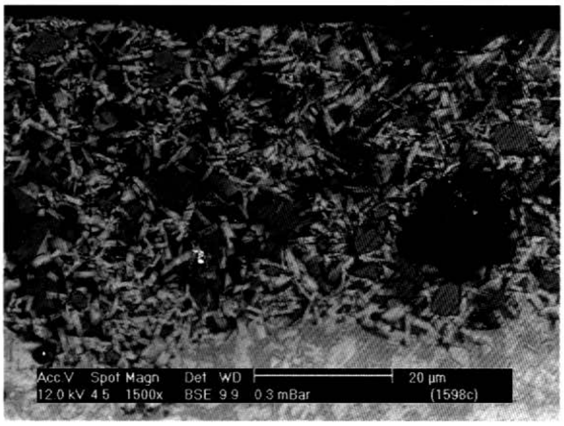

Figure 9. Cross section of S1B4 etched with HCl.

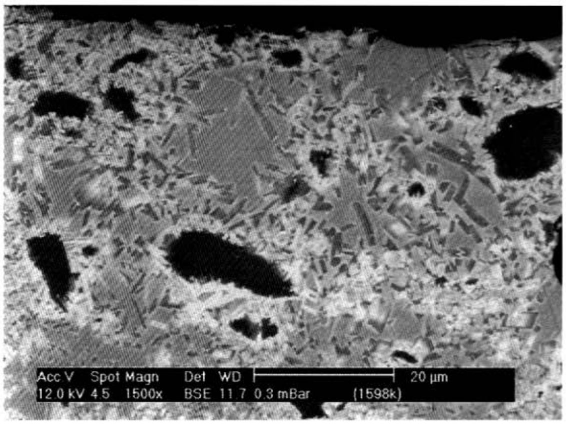

Figure 10. Cross section of glaze S1B4.

The glaze made with S2 is not attacked by either of the two acids. At the surface (Figure 11) a high proportion of zircon crystals and residual glassy phase are observed, which are not attackable. In the cross section (Figure 12), an interaction band about 15 μm thick can be appreciated, where crystallisation of the barium aluminosilicates of base B4 has been inhibited. This interaction area, however, does not reach the surface of the piece and the chemical properties of the glaze are those corresponding to the screen print.

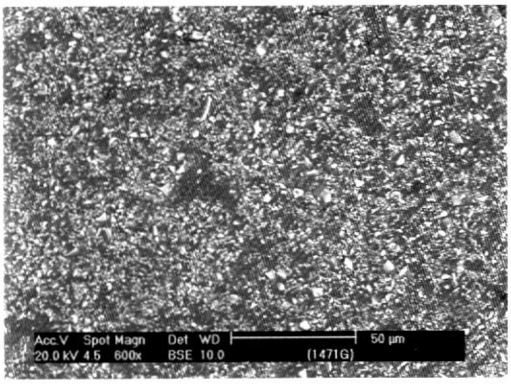

Figure 11. Surface of glaze S2B4.

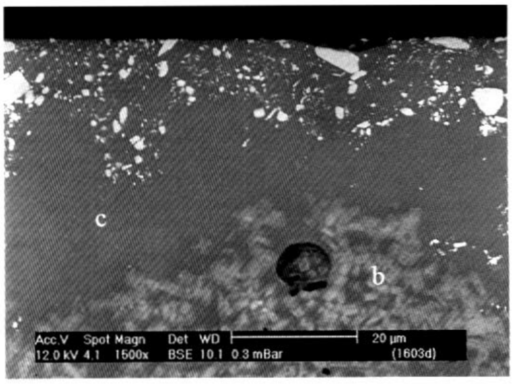

Figure 12. Cross section of S2B4; a) screen print, b) base, c) interaction region.

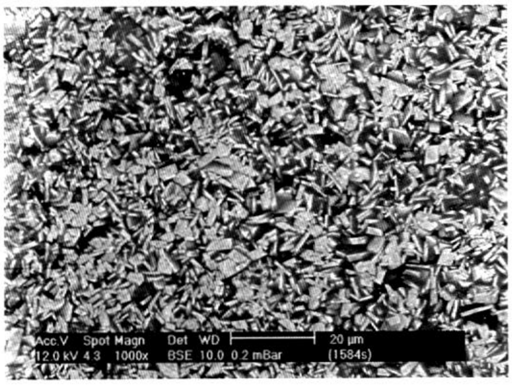

Figure 13. Surface of glaze S3B4.

The surface of the glaze produced with S3 (Figure 13) is full of barium aluminosilicates. In the attacked piece (Figure 14) some crystals seem to have been removed, though the glass aureole that surrounds them may have been attacked, facilitating their detachment. As a result of crystallisation, this glass can have been impoverished locally in silica in respect of the rest of the glassy matrix, which is not attacked. In fact, glass tendency to leach increases quickly with modifier content when the silica proportion falls below 66 mol%, a value at which every silicon atom is associated with a basic cation and significant rupture has occurred of the bonds in the glassy network [4].

The cross section (Figure 15) shows there has hardly been any interaction between the base and the screen print, owing to their compositional similarity and the low glassy phase content of both materials, which are highly crystallised. Unlike S1, acid attack has been restricted to the outer surface, without progressing inward into the glaze, which indicates that it occurs on scattered areas (crystals or aureoles of modified glass) and not on the continuous glassy matrix.

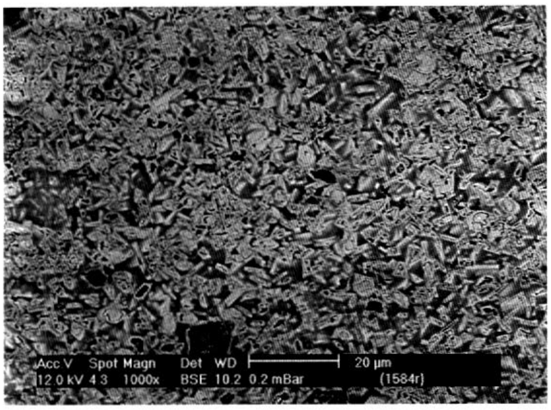

Figure 14. Surface of S3B4 etched with HCl.

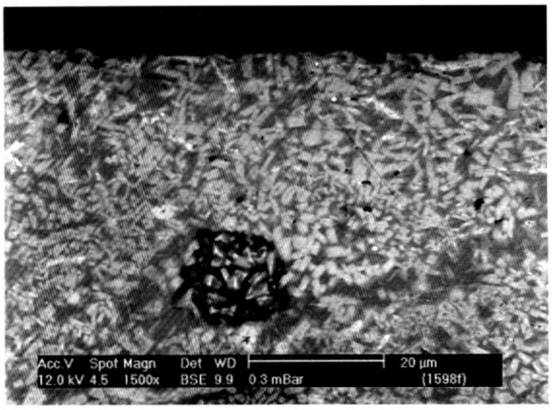

Figure 15. Cross section of S3B4 etched with HCl.

3.2.2 Effect of the base on the attackability of the resulting glazes.

To study the effect of the base glaze, screen print S1 was selected, which had been the most attackable in the previous experiments, and it was applied to bases B1 to B4.

Table 4 details the test results on the resistance to attack by hydrochloric and lactic acid.

Screen printing	Base	18% HCl	5% lactic acid
S1	B1	GHB	GHB
	B2	GHB	GHB
	B3	GHA	GHA
	B4	GHB	GHB

Table 4. Results of the acid resistance tests.

Figure 16 shows the surface appearance of the glazes produced on applying S1 to the different bases. Noticeable changes are observed in the microstructure of the glazed surface, implying that this screen print has interacted significantly with some of the bases.

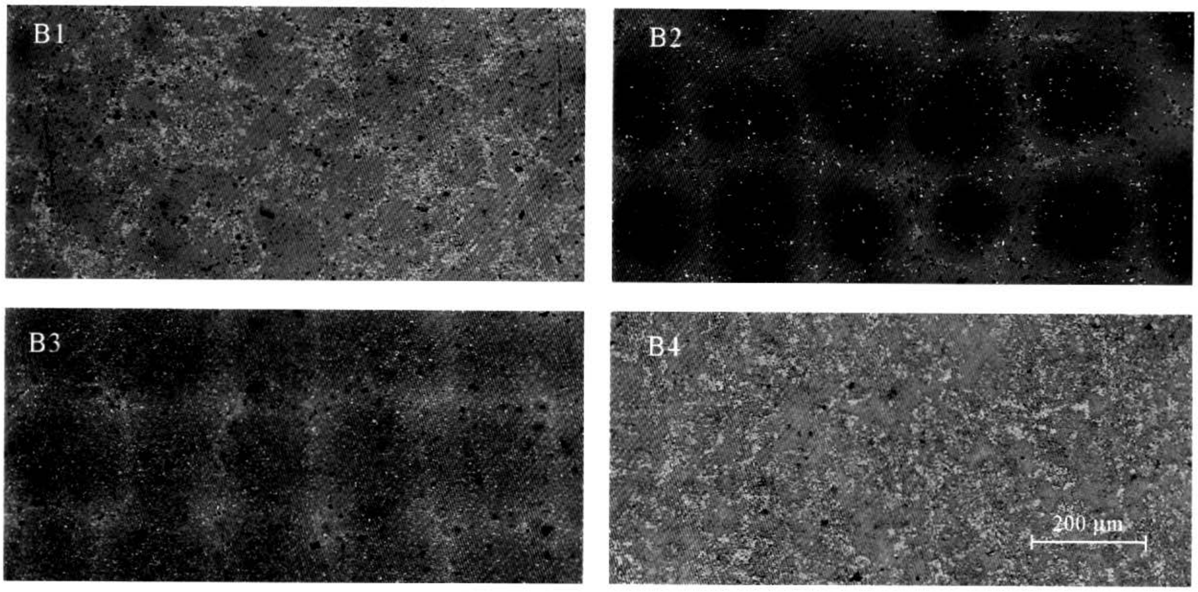

Figure 16. Surface of the glazes produced with screen print application S1 on bases B1, B2, B3 and B4.

The surface of the glaze made with base B1 (Figure 17) consists of a glassy matrix with barium aluminosilicates, together with quartz particles, kaolin and anorthite crystals. Attack (Figure 18) takes place on the anorthite crystals that have formed around the kaolin agglomerates, by reaction of kaolin with the calcium in the melt.

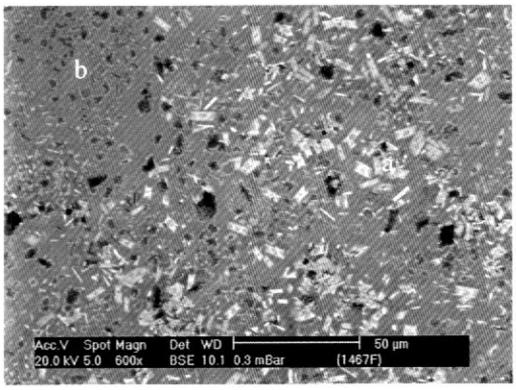

Figure 17. Surface of S1B1. a: barium aluminosilicates; b: kaolin/anorthite.

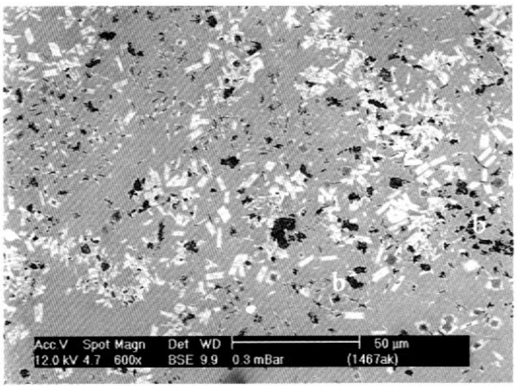

Figure 18. Surface of S1B1 etched with HCl. b: areas removed by attack.

In the polished cross section, the screen print completely covers base B1 (Figure 19), but the barium crystals only form in the uppermost part of the regions with less interaction with the base, since the compositional change that this causes inhibits crystallisation.

In the surface of the glaze made with base B2, zircon particles from the base can be observed (Figure 20). Areas with two colours can be distinguished: the clearer contain agglomerates of barium crystals and kaolin/anorthite particles, so that they will be the screen print areas interacting least with the base.

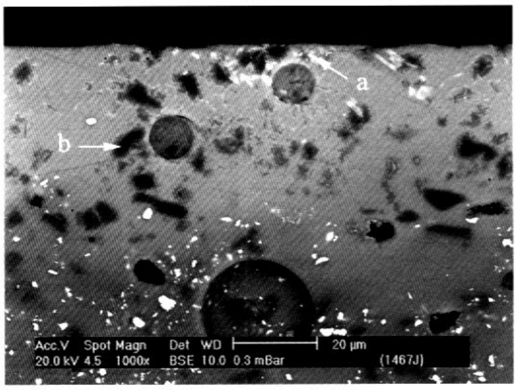

Figure 19. Cross section of S1B1. a: barium crystals; b: kaolin/anorthite.

The acid attack mainly eliminates anorthite crystals (Figure 21) and occurs in the areas with least interaction with the base (in the rest, they have sunken). The areas exhibiting greatest interaction with the base have not suffered attack, indicating improved base B2 behaviour. The most reasonable explanation is that the screen print has covered base areas that were attacked (alumina particles), as can be appreciated in the cross section (Figure 22).

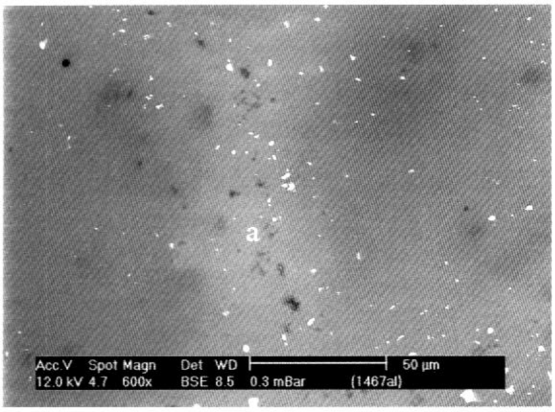

Figure 20. Surface of glaze S1B2.

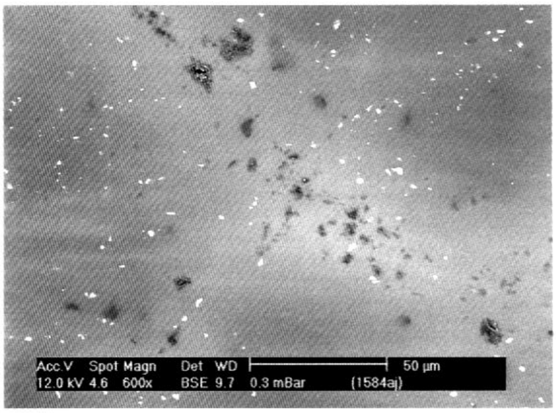

Figure 21. Surface of S1B2 etched with HCl.

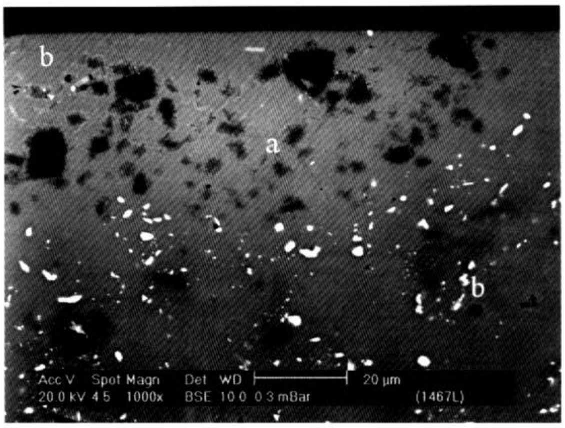

Figure 22. Cross section of S1B2 etched with HCl. a: screen print; b: base.

In the surface of glaze S1B3, two areas with different colours can also be distinguished; again, the clearer regions correspond to the smallest screen print interaction with the base (they contain some barium aluminosilicates). Crystalline aggregates from the base (quartz and zircon) are found across the whole surface, as well as acicular crystals of devitrified zircon from the base glaze frit (Figure 23). The cross section (Figure 24) again shows that the glaze surface is almost wholly covered by zircon and that the kaolin/anorthite agglomerates are inside the glaze, since the screen print has sunken and is covered by the base. The behaviour of S1B3 on exposure to acid attack is excellent, just as that of the base.

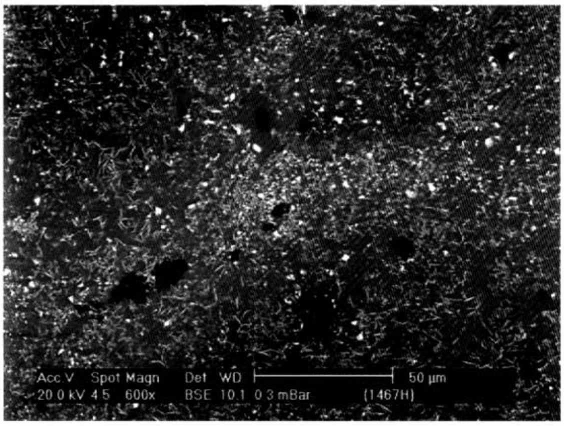

Figure 23. Surface of glaze S1B3.

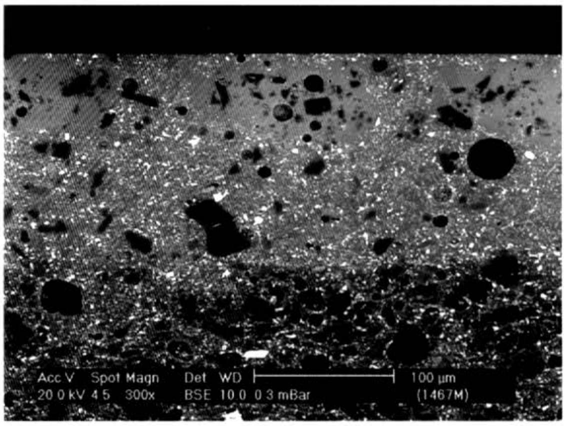

Figure 24. Cross section of glaze S1B3.

Finally, as set out above in the previous section, the glaze produced by application onto B4 is found to be readily attackable by the two acids that produce leaching of the glass throughout the entire thickness of the screen print. The photomicrographs of the surface and cross section (Figures 7 and 8) show that the quantity of arising crystals in S1 on applying it to B4 is much larger than when it is applied on the remaining bases, which indicates practically no interaction with B4, while S1B4 appearance and behaviour approach those that screen print S1 would have if a thicker layer were applied, without a base glaze. With the three previous bases, whose composition is quite different from that of S1, barium phase crystallisation is inhibited, the inhibition being greater as interaction between base and screen print increases. As a result of this smaller crystallisation, the residual glass contains more silica and is less attackable, so that acid attack is restricted to relatively sensitive crystalline phases, such as anorthite.

3.3. GLAZES PRODUCED BY WET APPLICATION

To evaluate the extent of the interaction between the glazes, the matt barium glaze (B4) was selected as a base onto which aqueous suspensions of two different glazes (C1 and C2) were applied with a bell. Glaze C1 consists of a mixture of matt barium frit with crystalline raw materials additions (wollastonite, feldspar, etc.); glaze C2 is a mixture of those same raw materials with a transparent frit.

The cross section shows that practically no interaction occurs in glaze B4C1 between the two applied layers.

In the case of glaze B4C2, given its compositional difference, an interaction region of about 30 μm is noticeable between both layers. In that area (Figure 25) glass colour is clearer than in that of the top layer, because it has been enriched in barium from the base and barium phase crystallisation has been inhibited.

Due to the great thickness of the bell applications (250μm), the interaction area is not very likely to reach the proper surface. Consequently, glaze resistance to acid attack will coincide with that of the top layer, and will only be affected if the glaze thickness covering this interaction area is eliminated during the polishing processes.

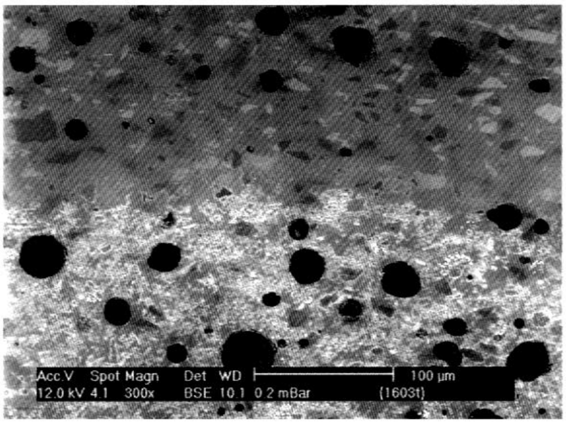

Figure 25. Cross section of glaze C2B4.

3.4 GLAZES MADE BY DRY APPLICATION AS GRANULARS

To study the interactions during firing among melts with different compositions, two granulars were applied onto base B4. One of the granulars (G1) was made from a frit containing zirconium and a high proportion of calcium and the other (G2) from a matt barium frit, similar to the one used in screen print S3. The resistance to acid attack was evaluated in the resulting glaze and in the glaze produced on polishing the piece in a laboratory facility, since many granular applications are polished.

Figures 26 and 27 show the surface of the glaze produced with granular G1, respectively before and after polishing. The non-polished glaze (Figure 26) contains four types of crystals: a) ZrO_2, very clear and very small crystals with a rhombic form, b) zircon, clear acicular crystals, also of a small size, c) double silicate of calcium and zirconium, with large size acicular crystals, arranged radially forming a six-pointed star and, finally, d) wollastonite, darker, and arranged in an X shape. The smooth dark areas are glassy phase.

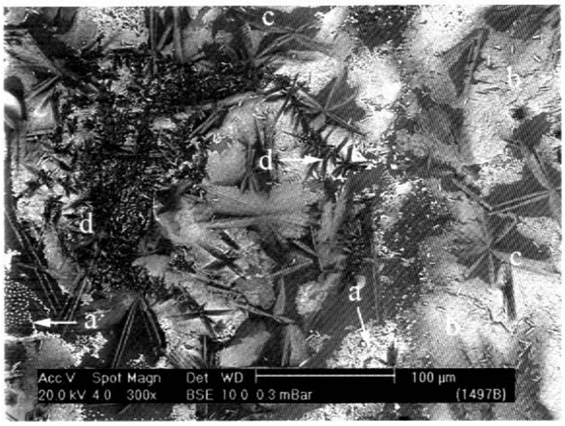

Figure 26. Surface of non-polished granular G1. a: zirconia; b: zircon; c: calcium and zirconite double silicate.

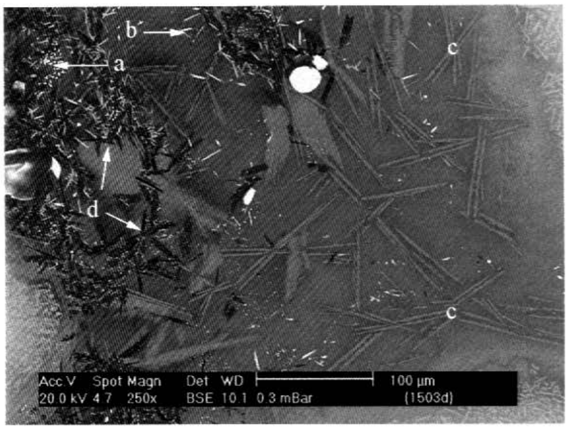

Figure 27. Polished surface of G1.

In the surface of the polished glaze (Figure 27), the crystals of the calcium and zirconium double silicate predominate, distributed throughout what were the initial granular particles. However, the ZrO_2, $ZrSiO_4$ and wollastonite crystals are located at the interfaces (outside surface of what were initially granular particles or cracks in the particles). The right half of Figure 27 corresponds to the centre of the granular particle, which only contains calcium and zirconium double silicate crystals. The left half corresponds to what was the granular particle boundary and this is where the surface crystallising phases such as wollastonite, ZrO_2 and $ZrSiO_4$ are found.

On etching the non-polished and polished glazes with 18% ClH, it was observed that:

a) The non-polished G1 granular areas suffered no acid attack, except the wollastonite crystals, which were eliminated (Figure 28).

b) The polished G1 granular (Figure 29) is not attacked, except for the wollastonite crystals, which also underwent attack in the non-polished glaze.

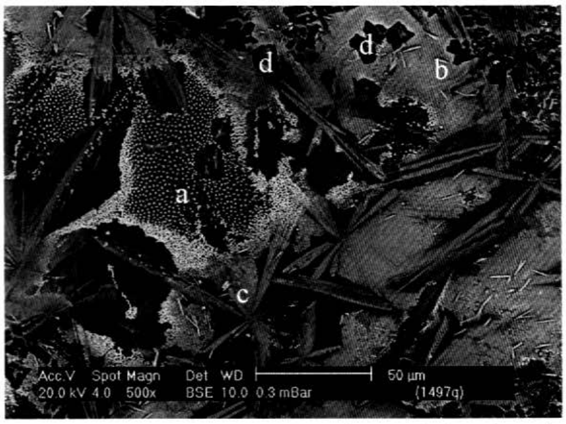

Figure 28. Non-polished surface of G1, etched with HCl.

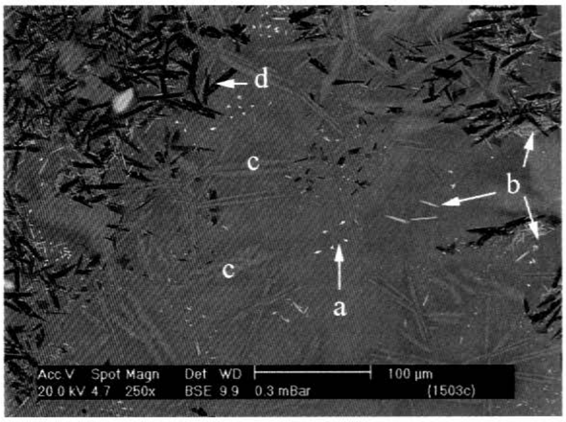

Figure 29. Polished surface of G1, etched with HCl.

These results indicate that the residual glassy phase of granular G1 is highly resistant to acid attack, probably because it contains a large proportion of non-crystallised ZrO_2 and this increases the resistance to acid attack. The ZrO_2 remains in the glassy phase because these phases crystallise superficially, and due to the large particle size of the granular, ZrO_2 diffusion toward the surface, to crystallise, has not been completed. Figure 30 shows a cross section of this glaze, in which zircon crystals mark the contours of what were initially granular particles.

If the frit is applied in an aqueous suspension, appropriately milling granular G1, the fraction of crystallising zirconium increases in the resulting glaze, with the ensuing zirconium impoverishment in the glassy phase and decreased resistance to acid attack. In fact, the resulting glaze is attacked by hydrochloric acid, by leaching of the modifier cations in the glassy phase. Figure 31 depicts a cross section of the glaze produced by wet application of frit G1, showing that it contains more zircon, and calcium and zirconium double silicate than the glaze made by applying the granular.

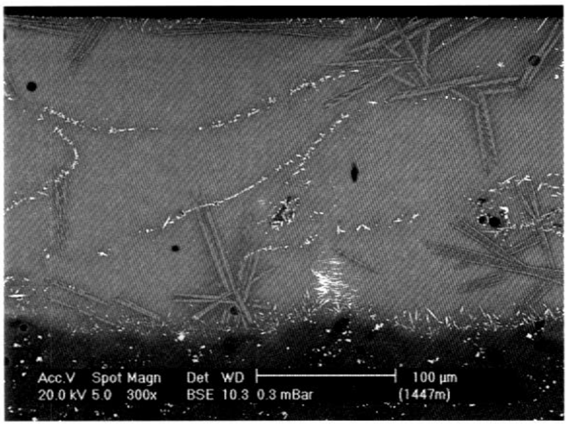

Figure 30. Cross section of the glaze produced with granular G1.

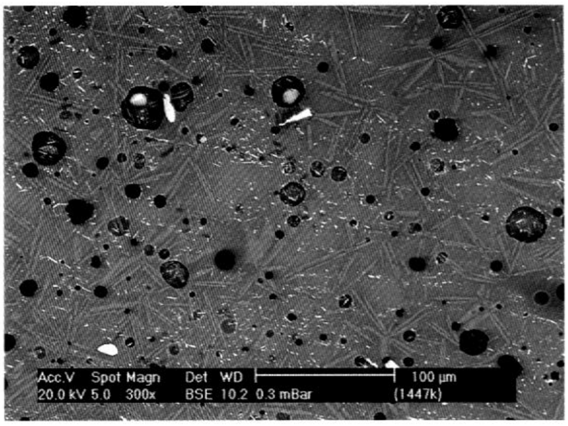

Figure 31. Cross section of the glaze produced with small size G1 particles.

If the glaze polishing process is not carried out with laboratory polishers, but with industrial equipment, the resistance to acid attack decreases markedly. This could partly occur because the scratches and chipping arising in industrial polishing considerably increase the contact surface between the glaze and the acid[13]. Even without a significant increase in contact surface occurring, relatively small scratches can cause quick corrosion of the glass if the glass is soluble (albeit lightly) in the attacking solution, and development of deep grooves inwards into the glaze [4].

Granular G2 microstructure and behaviour differ considerably from those described for G1. At the surface of the glaze corresponding to what were initially G2 granular particles, a great quantity of barium aluminosilicate crystals are observed (celsian or barium orthoclase crystals), as well as a relatively small glassy phase fraction (Figure 32).

On polishing this glaze (Figure 33) crystallisation is also found to be superficial and the crystals are not uniformly distributed, so that some areas are full of crystals while others contain more glassy phase.

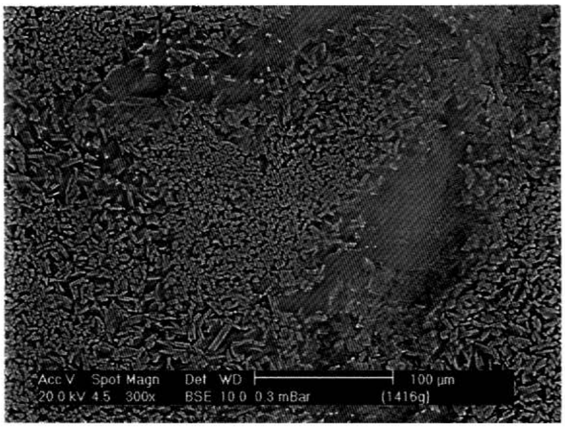

Figure 32. Surface of non-polished granular G2.

In the cross section of the glaze, the particle interiors are observed to contain a smaller density of crystals, so that the quantity of crystals at the polished glaze surface will depend on the thickness of the layer removed in the polishing process (Figure 34).

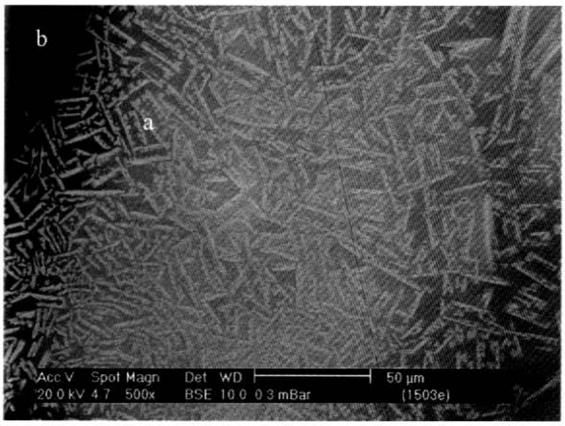

Figure 33. Surface of granular G2. a: SiAlBa; b: glassy phase in the interaction region.

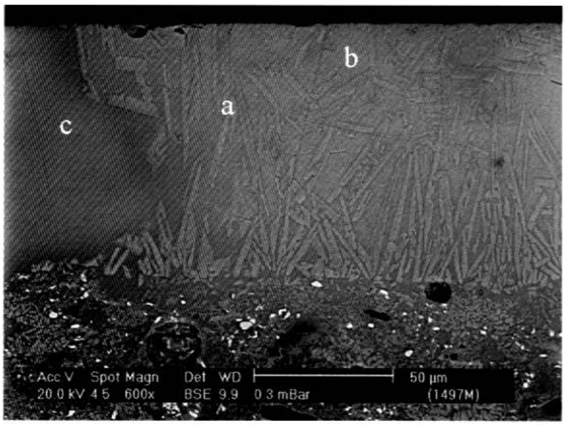

Figure 34. Cross section of granular G2. a: SiAlBa; b: glassy phase; c: contact area with G1.

Behaviour of this glaze on exposure to acid attack depends on whether the surface is polished or not. In the non-polished glaze, very slight attack occurs in the glassy phase coating the crystals, as shown in Figure 35. This attack is not appreciated visually in the piece. In the case of the polished glaze, the glassy phase inside what was initially a granular particle is leached with HCl, leaving a silica skeleton (Figure 36). The glassy phase of what was initially the granular boundary is attacked much less, which will be the result of a change in composition. The explanation is likely to lie in the fact that on having more barium aluminosilicates in this area, the glassy phase is poorer in alkalis and alkaline earths, increasing its chemical resistance. Another possibility is that at the granular border an interaction has occurred between what were initially a G2 particle and a G1 particle, which is much more resistant to acid attack.

It was observed that in the polished glaze, the initially smaller size G2 granular particles have not been attacked by the acid. This can be due to the two possible reasons mentioned previously: in the smaller size granular particles, there is a greater overall crystal density, while furthermore, owing to their small size, the interaction area with G1 granular particles is greater.

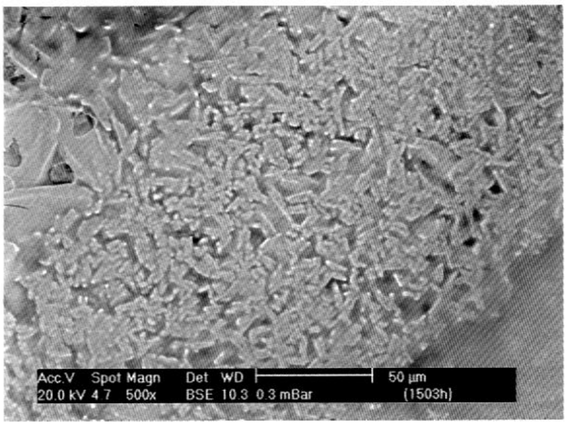

Figure 35. Surface of non-polished G2, etched with HCl.

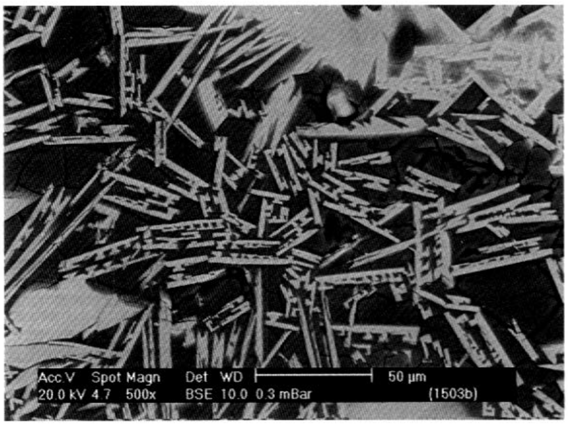

Figure 36. Surface of polished G2, etched with HCl.

The interaction that takes place between the two granulars can be observed in Figure 37.

It shows that crystallisation is inhibited in the contact areas between G1 and G2, and the resulting glass has an intermediate colour between that of G2 (clearer with signs of backscattered electrons, due to the high barium content) and that of G1, which implies an intermediate composition and, consequently, a high degree of reaction between both melts. These reaction regions have shown themselves to be resistant to acid attack both in polished and non-polished areas, possibly because the glassy phase has zirconium from G1 and a more balanced composition of network formers and modifiers (owing to diffusion and inhibited crystallisation).

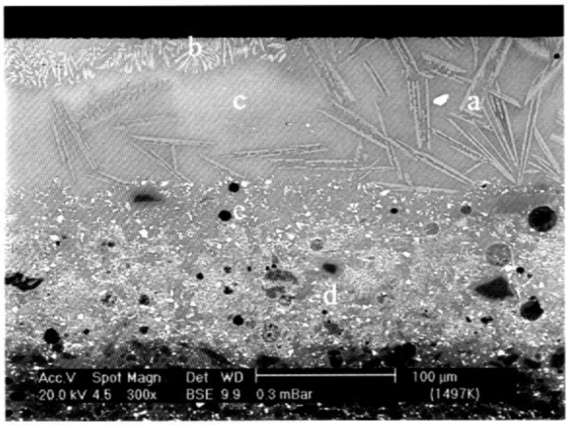

Figure 37. Cross section of the glaze produced with G1 and G2. a: granular G1; b: granular G2; c: interaction of G1 and G2; d: base B4; e: interaction of G1 and B4.

4. CONCLUSIONS

a) In the glazes studied in this work it has been shown that acid attack can take place on the glassy phase (leaching modifier cations and leaving a crazed siliceous skeleton) and on the crystalline phases. In these glazes, the most attackable crystalline phases were shown to be wollastonite and anorthite. The great variety of acid attack manifestations makes it difficult to predict the behaviour of a devitrifying frit or a frit that interacts with other glaze components.

b) The effect of lactic acid has been similar in every case to that of HCl, though less aggressive, so that the attack mechanism seems to be related to the presence of protons and not to a chelating effect on the divalent cations. However, these results cannot be considered generally applicable.

c) Of the glazes made with the base glazes, the most resistant to acid attack were B1 and B3, with high zirconium contents. Base B4 suffered slight acid attack on the glassy phase. Base B2 would not be attackable, if it did not contain porous agglomerates of alumina, which increase the surface area exposed to acid and locally modify the composition of the surrounding glass as a result of their partial dissolution.

d) In every case, the interaction between the base glazes and the materials applied to them rose as the compositional difference increased and their melt viscosity decreased (favouring diffusion processes).

e) The screen printing application is most likely to present variations in behaviour by interaction with the base, due to its small layer thickness. On applying different screen prints to base B4, little interaction was observed, so that the resistance to acid attack is only determined by the properties of the screen print outside layer. The only interaction observed with B4 is that of screen print S2, but it does not affect glaze behaviour, since the interaction area is not exposed to acid attack. Screen print S1 interacts with all the bases except B4, whose composition is closest to S1. The appearance and behaviour of glaze S1B4 approaches those that screen print S1 would have if it were applied in a thicker layer, without base glaze. The interaction of S1 with the rest of the bases makes the quantity of arising crystalline phases decrease and the residual glass more resistant to acid attack, so that glaze behaviour improves with regard to that of screen print S1. In one case (S1B2), resulting glaze resistance to acid attack exceeds that of its individual components (S1 and B2), since as a result of the screen print sinking into the base, particles of kaolin/anorthite from B2 are drawn inside, making it attackable.

f) In the glazes applied by a bell, interaction will be restricted to a more or less wide area around the interface (depending on melt viscosity) and will not modify the resistance to acid attack unless this area surfaces in the glaze polishing process.

g) In the glaze formed with the granulars, there are also interaction regions, which can be distinguished because G2 crystallisation was inhibited, due to the change in composition. With regard to acid attack, granular G1 is found to be resistant (except for the elimination of wollastonite crystals), both when polished and non-polished, while polished granular G2 is attacked by leaching of the glassy phase. The interaction areas of G2 with G1, however, are not attacked by these acids even after polishing.

5 REFERENCES

[1] ISO 10545-13. Ceramic tiles-Part 13: Determination of chemical resistance.

[2] OHTA, H,; SUZUKI, Y., Chemical durability of glasses in the systems SiO_2-CaO-Na_2O-R_mO_n, *Ceram. Bull.*, 57(6), 602-604, 1978.

[3] SCHOLZE, H., Chemical durability of glasses, *J. Non-Cryst. Solids*, 52, 91-103, 1982.

[4] NEWTON, R.G. The durability of glass - a review. *Glass Technology*, 26 (1), 21-38, 1985.

[5] BACON, F.R.; RAGGON, F.C.; Promotion of attack on glass and silica by citrate and other anions in neutral solution. *J. Am. Ceram. Soc.*, 42(1), 199-205, 1959.

[6] PAUL, A.; YOUSSEFI, A. Influence of complexing agents and nature of buffer solution on the chemical durability of glass. Part 2: effect of EDTA, ethyl alcohol, and sugar in the leach solution. *Glass Technol.*, 19(6), 166-170, 1978.

[7] PERERA, G.; DOREMUS, R.H. Dissolution rates of commercial soda-lime and Pyrex borosilicate glasses: influence of solution pH. *J.Am.Ceram. Soc.* 74 (7) 1554-58, 1991.

[8] COOKE, D.; PAUL, A. Chemical durability of glass enamels containing B_2O_3. Part 2: Lead borosilicates containing MgO, CaO, ZnO, Al_2O_3, TiO_2 and ZrO_2. *Trans. J. Br. Ceram. Soc.*, 77(4), 116-120, 1978.

[9] FERNÁNDEZ NAVARRO, J.M.; MARI, E.A.; Influencia de la adición de ZrO_2 y TiO_2 sobre el comportamiento químico de vidrios de silicato y borosilicato sódico-cálcico. *Bol. Soc. Esp. Ceram. Vidr.*, 29(4), 235-244, 1990.

[10] HERNÁNDEZ, J.A.; OTEO, J.L. Reacciones de la superficie del vidrio con soluciones acuosas. *Bol. Soc. Esp. Ceram. Vidr.* 21(2), 81-96, 1982.

[11] CALESTANI, G.; MONTENERO, A.; FERRAGUTI, E; INGLETTO, G.; BETTINELLI, M. Influence of some oxides on the durability of a borosilicate glass. *J. Non-Cryst. Solids*, 84, 452-462, 1986.

[12] OKA, Y.; TOMOZAWA, M. Effect of alkaline earth ion as an inhibitor to alkaline attack on silica glass. *J. Non-Cryst. Solids*, 42(1-3), 535-544, 1980.

[13] FERNÁNDEZ NAVARRO, J.M. *El vidrio*, 2ª ed. Madrid: CSIC, 1991.

[14] DAS, C.R. Chemical durability of sodium silicate glasses containing Al_2O_3 and ZrO_2. *J. Am. Ceram. Soc.*, 64(4), 188-193, 1981.

[15] MITRA, N.K.; GANGOPADHYAY, T.K.; MUKHERJEE, P.; DEBNATH, S.K. Effect of substitution of zirconia on the chemical durability of alkali borosilicate glasses. *Indian ceramics*, 16(1), 7-10, 1972.

[16] ESCARDINO, A. Crystalline glazes. IV World Congress on Ceramic Tile Quality, 10-13 March, 1996. p. 87-110.