HIGH-TEMPERATURE MATT GLAZES WITH HIGH CHEMICAL RESISTANCE

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ABSTRACT

A great variety of matt glazes are currently available in the market, of which the calcium-based glazes are particularly noteworthy due to their widespread use. This type of glaze displays low resistance to chemical attack, especially by acids. Given the importance of having glazes with high chemical resistance for the manufacture of floor tiles, the present study has addressed the formulation of glaze compositions that yield transparent matt glazes in processes with high firing temperatures, which perform well under chemical attack.

The present study has determined the acid attack mechanisms in a transparent matt glaze for porcelain tile, obtained from a glaze composition containing a frit (with high CaO content) and other non-vitreous raw materials. The main cause of deterioration in this glaze was shown to be the presence of anorthite in the resulting glaze layer, an attackable crystalline phase in acid medium. The glaze composition was then modified, both in relation to the frit and to the nature of the other raw materials used. This yielded a transparent matt glaze from a glaze composition consisting of a frit (with high MgO content) and other raw materials. This glaze coating has high chemical resistance, owing to the presence of the cordierite crystalline phase, a magnesium phase that is resistant to acid attack.

1. INTRODUCTION

At present calcium matt glazes are widely used, as opposed to other matt glazes such as those of barium or zinc. There are several reasons for this widespread use. These include, in particular, their lower price, the possibility of obtaining matt glazes with high transparency compared with the zinc matt glazes, and the use of non-toxic raw materials in fabricating these, compared with the barium matt glazes.

In processes where high firing temperatures are used, as is the case of the manufacture of glazed porcelain tile, matt glazes can be obtained with high transparency using frits with high calcium content, in addition to other raw materials, such as feldspars and nepheline. However, these glazes tend to exhibit low resistance to acid attack, a key property if the tiles are to be used as flooring in aggressive environments.

One of the alternatives considered in the present study has been the formulation of magnesium matt glazes, i.e. glazes in which the matt effect is caused by crystalline phases that contain magnesium oxide. Most of the research in glazes with high magnesium oxide contents has been based on the oxide system SiO_2-MgO-CaO[1-3], SiO_2-Al_2O_3-MgO-CaO[4,5] or systems like this last one[6], in some cases seeking to obtain opaque white glazes as an alternative to zirconium white glazes[1-3,5].

Taking into account the phase diagram corresponding to the oxide system SiO_2-Al_2O_3-MgO[7], among the possible crystalline phases that contain magnesium oxide (protoenstatite: $MgO{\cdot}SiO_2$, forsterite: $2MgO{\cdot}SiO_2$, spinel: $MgO{\cdot}Al_2O_3$, cordierite: $2MgO{\cdot}5Al_2O_3{\cdot}2SiO_2$ and sapphirine: $4MgO{\cdot}5Al_2O_3{\cdot}2SiO_2$), there is one which, in principle, could give rise to matt glazes with high transparency. This crystalline phase is cordierite, which, due to its low refractive index (1.53-1.57)[8], could give rise to transparent glazes. Certain studies report the feasibility of obtaining glazes with cordierite devitrifications in the systems SiO_2-Al_2O_3-MgO[9,10] and SiO_2-Al_2O_3-MgO-CaO[5], and suggest that the characteristics of this crystalline phase could provide the resulting glazes with good properties.

2. OBJECTIVE

The objective of this study has been to improve the chemical resistance of a transparent matt glaze for porcelain tile by developing glaze compositions prepared from frits with high magnesium oxide content. The starting matt glaze composition, designated S, is made up of a frit of the system SiO_2-Al_2O_3-K_2O-CaO-MgO and other crystalline raw materials, its composition being (% by weight): 56.2 SiO_2-20.7 Al_2O_3-13.7 RO-9.4 R_2O.

3. EXPERIMENTAL

The different tested frits were obtained by fusing the raw materials in an electric kiln, at a peak temperature of 1600ºC and 30 min. dwell time at this temperature. The frit was obtained by quenching the melt in water at ambient temperature. The glazes were prepared from the frits and other crystalline raw materials by wet milling, using the necessary additives (binder and deflocculant) to allow correct application.

The glazes were applied onto a green porcelain tile body, and the glazed pieces were fired in an electric laboratory kiln at a peak temperature of 1180ºC. The chromatic coordinates of the fired glazed pieces were determined with a spectrophotometer, using illuminant C and 2º standard observer. Gloss was determined with a reflectometer, at a 60º angle of incidence. Glaze transparency was quantified by calculation of parameter TP, defined as the quotient between the reflectance of the body and the reflectance of the glazed piece, both fired at 1180ºC. The closer this quotient approaches unity, the more similar will the colour of the finished piece be to the colour of the body and, therefore, the more transparent will the glaze be.

The chemical resistance of the glazed pieces was determined according to standard UNE-EN ISO 10545-13. The test time was four days, and the reagents tested were strong acids and alkalis: hydrochloric acid (18% v/v), lactic acid (5% v/v) and potassium hydroxide (100g/l). The classification of the attack was made according to the method set out in the above standard. In addition, the surface of the pieces subjected to attack was observed by scanning electron microscopy.

The microstructural characterisation of the glazes was performed by observation of the glaze surface and cross-section with a scanning electron microscope (SEM), fitted with an energy-dispersive X-ray microanalysis (EDX) system. The crystalline structures present in the glazes were identified by X-ray diffraction; for this, glaze test specimens were prepared and fired at 1180ºC, using the same thermal cycle as the one applied to obtain the glazed pieces.

4. CHARACTERISTICS OF STARTING GLAZE S

Table 1 details the colour and gloss of the pieces obtained from glaze S. For comparative purposes, it also indicates the colour of the porcelain tile body fired at the same temperature (1180ºC), used to calculate transparency (TP).

REFERENCE	L*	a*	b*	GLOSS 60º	TP
Body	75.31	1.86	13.90	--	--
Glaze S	82.56	1.10	6.09	9	0.77

Table 1. Chromatic coordinates and gloss of the pieces of porcelain tile fired at 1180ºC

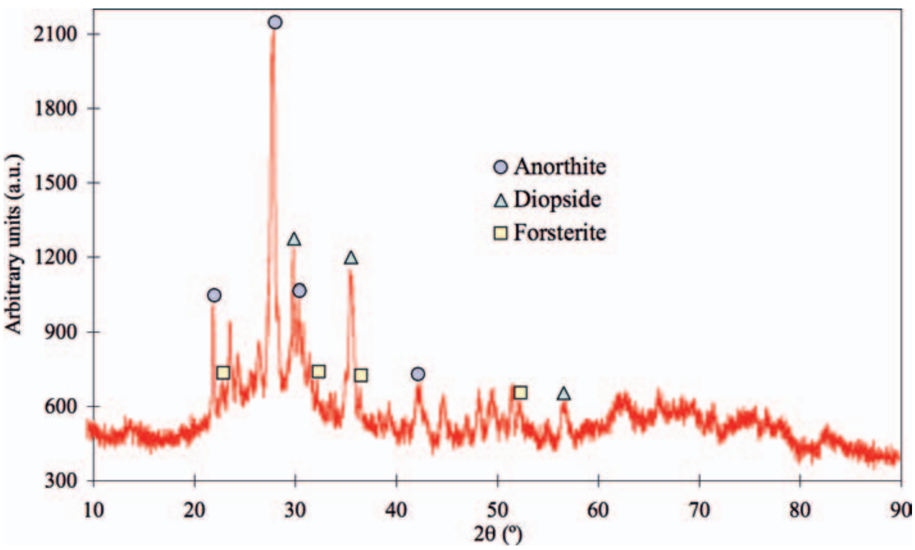

Figure 1. Diffractogram of glaze S. 1180ºC.

The following crystalline phases were identified by X-ray diffraction (XRD) in the glaze obtained at 1180ºC: anorthite (**An:** $CaAl_2Si_2O_8$) and diopside (**D:** $CaMgSi_2O_6$), in addition to forsterite (**F:** Mg_2SiO_4) as a minor phase. Figure 1 depicts the diffractogram obtained for this glaze, in which it can be observed that the sample is composed of glassy phase and the three foregoing crystalline phases, of which anorthite is the major crystalline phase.

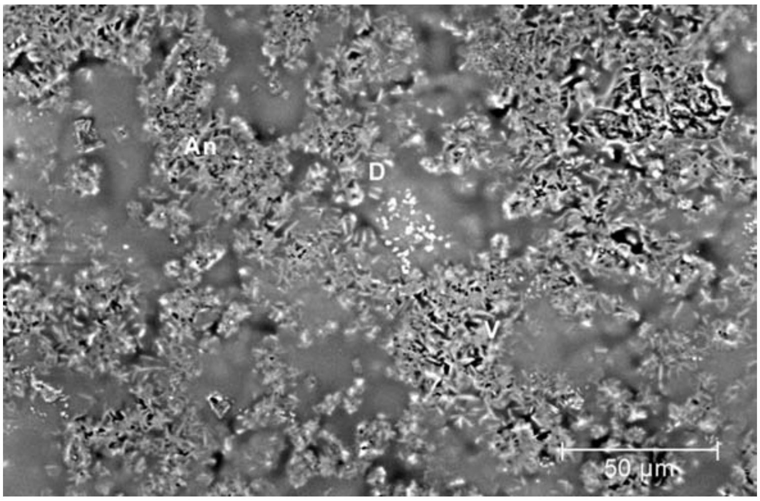

Figure 2. Surface of the piece obtained with glaze S. 1180ºC

Figure 2 shows the photograph corresponding to SEM observation of the glaze surface. It is observed to contain glassy phase (V) and two crystalline phases, anorthite (An) and diopside (D), anorthite being the major crystalline phase. Anorthite is a crystalline phase that has a low refractive index (1.58)[8] and, therefore, does not provide the glazes that contain it with high opacity.

Figures 3 and 4 show a cross-section of the glaze, displaying lighter-coloured regions that correspond to areas where devitrification has taken place. These regions can be classified in terms of their appearance and analysis in two types: the ones marked An in Figure 3 correspond to anorthite, whereas the ones marked D in this figure corresponds to diopside.

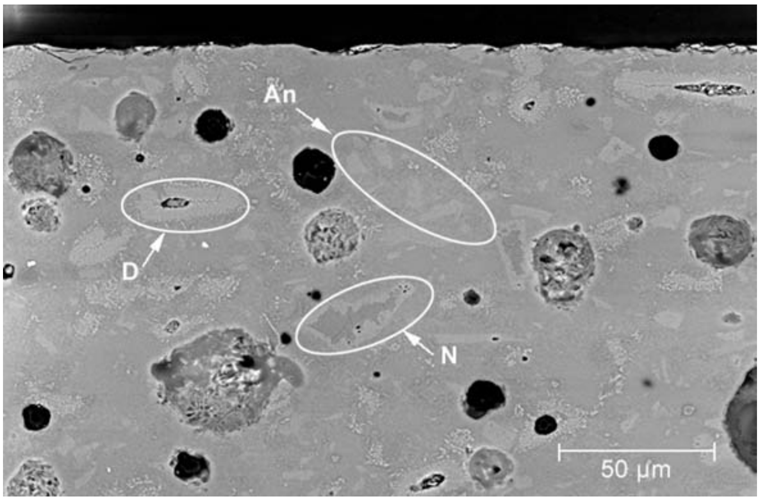

Figure 3. Cross-section of glaze S. 1180ºC.

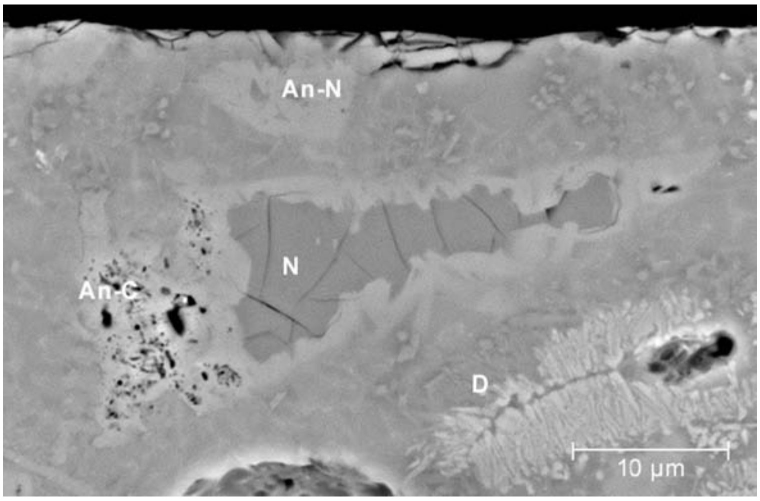

Figure 4. Cross-section of glaze S. 1180°C.

Darker-coloured regions can also be observed in Figure 3. Analysis of these regions indicates that nepheline particles (N) are involved (nepheline being a raw material used in glaze preparation), while the surface exhibits a crust which analysis showed was anorthite. This indicates that the regions corresponding to anorthite appear to proceed from the reaction of nepheline with the CaO present in the glassy phase. Figure 4 shows in greater detail the partly reacted nepheline particles (N), which have an anorthite crust, and the totally reacted nepheline particles (An-N), whose analysis indicates that anorthite is involved, as well as kaolin particles, which have also reacted with the glassy phase to form anorthite (An-C). Figure 4 also shows with greater clarity one of the regions in which diopside devitrification has taken place (D).

Table 2 sets out the results obtained after subjecting the glaze to the test for determining the chemical resistance to high concentration acids and alkalis. According to the classification, the main deterioration occurs when the glaze is subjected to acid attack.

The surface of the zones subjected to attack was observed by SEM, and the resulting photographs are depicted in Figures 5-7. These photographs show that acid attack eliminates anorthite mainly in the areas where it had formed by reaction with nepheline particles (An-N). This attack is more pronounced for hydrochloric acid.

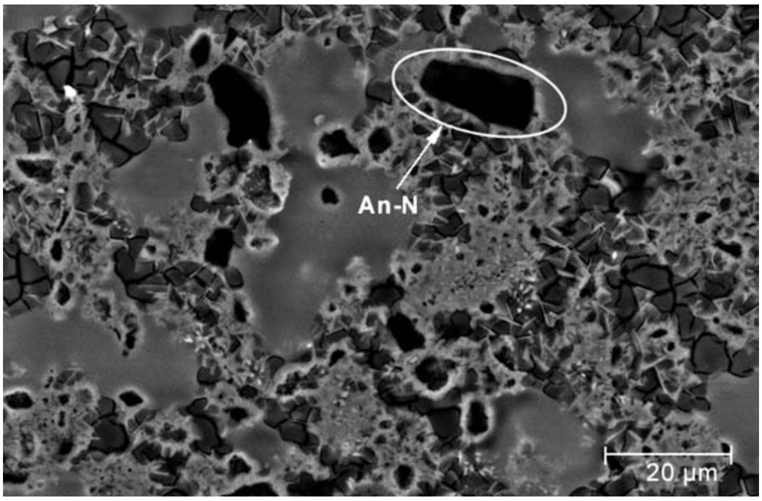

Figure 5. Surface of glaze S attacked with HCl.

Reagents	Classification according to the standard
Hydrochloric acid 18%	GHB
Lactic acid 5%	GHB
Potassium hydroxide 100 g/l	GHA

Table 2. Chemical resistance of glaze S.

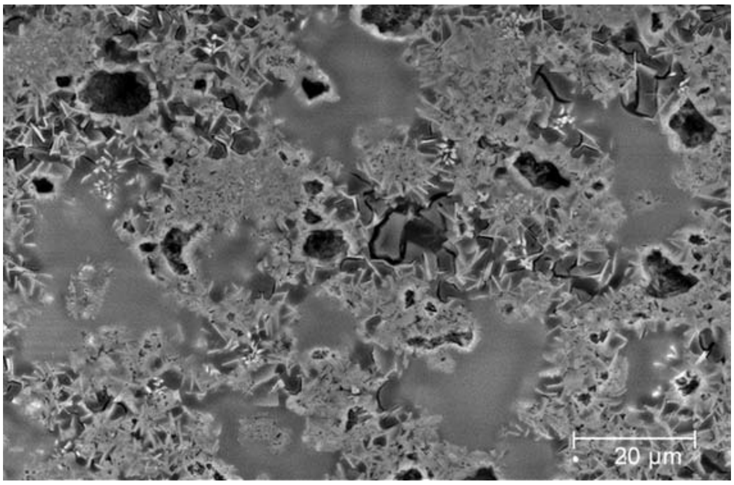

Figure 6. Surface of glaze S attacked with lactic acid.

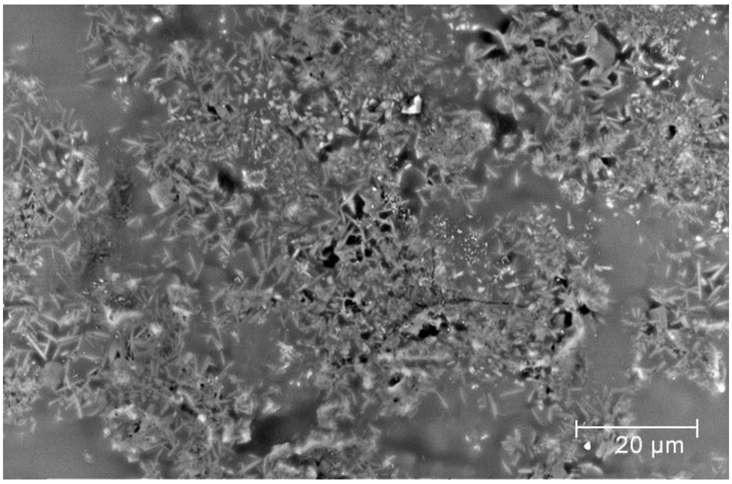

Figure 7. Surface of glaze S attacked with KOH.

5. DEVELOPMENT OF NEW FRIT COMPOSITIONS

The objective of this part of the work was to obtain frit compositions that yielded glazes in which species would devitrify that contained Mg in their composition. As already mentioned in the introduction, in the system SiO_2-Al_2O_3-MgO, the devitrifiable crystalline species with the lowest refractive index is cordierite. For this reason, different frit compositions were tested, in an attempt to obtain glazes in which this phase would devitrify.

5.1. VARIATION OF THE MGO/RO RATIO

Two frit compositions were obtained (M and M1), just varying the MgO/RO ratio, by weight, while holding the proportion of the different oxides that make up reference glaze S. In reference glaze S the MgO/RO ratio was 0.37, whereas in frit M the MgO/RO ratio was 1.0, i.e. only MgO was used as an alkaline-earth oxide, and in frit M1, this was 0.63. Table 3 summarises the results obtained. It lists the values of the chromatic coordinates, gloss, transparency and the crystalline phases present in the glazes obtained from the frits at the working temperature, 1180ºC, compared with those obtained for the reference glaze.

The data indicate that the presence of calcium oxide in the composition favours anorthite formation, and that the progressive increase in magnesium oxide causes crystalline phases containing Mg to appear. However, in the composition with a high percentage of magnesium (M), the proportion of crystalline phases present is very low, and glossy glazes are produced.

	GLAZE S	M	M1
MgO/RO	0.37	1.0	0.63
L*	85.6	85.5	84.8
a*	1.10	0.50	0.41
b*	6.09	3.34	4.10
TP	0,77	0,70	0,72
Gloss 60º	9	95	7
Crystalline phases	Anorthite: $CaAl_2Si_2O_4$ Diopside: $CaMgSi_2O_6$ Forsterite^M: Mg_2SiO_4	Forsterite^M Mg_2SiO_4 Pyrope^M : $Mg_3Al_2Si_3O_{12}$	Anorthite: $CaAl_2Si_2O_4$ Forsterite^M: Mg_2SiO_4

^{M} *Minor phase.*

Table 3. Characterisation data of the glazes obtained from the different test frits.

5.2. VARIATION OF THE AL_2O_3/MGO RATIO

Since cordierite is a species that contains Al_2O_3 in its composition, with a view to favouring cordierite formation we raised the Al_2O_3/MgO ratio in the frit composition in which anorthite devitrification did not occur (composition M), testing frit composition AM, indicated in Table 4. This table sets out the characterisation data of the glaze obtained from the frit at 1180ºC.

The increase in alumina content encouraged the formation of species containing Al and Mg (spinel and cordierite). However, spinel formation was favoured more than cordierite formation, giving rise to less transparent glazes, possibly because the spinel has a greater refractive index (1.72)[8]. In view of this, and taking into account that, according to the literature[5,11], cordierite formation depends on the type of fluxing oxide used, this variable was modified in the composition of frit AM.

	M	AM
Al_2O_3/MgO	1.5	2.4
L*	85.5	87.5
a*	0.50	0.21
b*	3.34	1.68
TP	0.70	0.66
Gloss 60º	95	21
Crystalline phases	Forsterite^M Pyrope^M	Forsterite Spinel Cordierite^M

Cordierite: $Mg_2Al_4Si_5O_{18}$, Spinel: $MgAl_2O_4$, Forsterite: Mg_2SiO_4, Pyrope: $Mg_3Al_2Si_3O_{12}$
^{M}: Minor phase

Table 4. Characterisation data of the glazes obtained from the tested frits

5.3. VARIATION OF THE TYPE OF FLUX (R_2O, B_2O_3)

The main fluxes of composition AM were Na_2O and K_2O. Therefore, the proportions of these two oxides were modified and other fluxes were used, like Li_2O and B_2O. Table 5 lists the resulting compositions, and also details the characterisation data of the glazes obtained from these compositions at 1180ºC.

Figure 8 shows the diffractograms obtained for the different glazes, in which the peaks corresponding to the major crystalline phases have been marked. The results indicate that cordierite formation from this frit is favoured when boron oxide is used as a flux; glazes are thus produced with higher transparency. The use of alkaline oxides as fluxes encourages the formation of spinel and forsterita, species whose greater refractive indices give rise to less transparent glazes.

The only problem detected in the glaze obtained from frit AMB is that, due to the high proportion of boron oxide, pinholes appear in the surface of the glaze obtained at 1180ºC.

	AM	AML	AMB	AMN	AMK
B_2O_3, R_2O	R_2O=9.5%	Li_2O=5.6%	B_2O_3=9.5%	Na_2O=9.5%	K_2O=9.5%
L*	87.5	87.5	83.8	87.9	87.5
a*	0.21	-0.24	0.31	-0.01	0.41
b*	1.68	1.40	5.08	1.81	0.88
TP	0.66	0.66	0.74	0.65	0.66
Gloss 60º	21	17	24	23	18
Crystalline phases	Forsterite Spinel Cordierite^M	Spodumene Spinel^M Cordierite^M	Cordierite Mullite Magnesium silicate^M	Spinel Forsterite^M Cordierite^M	Spinel Cordierite Mullite Forsterite^M Leucite^M

Cordierite: $Mg_2Al_4Si_5O_{18}$, Spinel: $MgAl_2O_4$, Spodumene: $LiAlSi_2O_6$, Forsterite: Mg_2SiO_4, Mullite: $Al_6Si_3O_{15}$,
Magnesium silicate: $MgSiO_3$, Leucite: $K(AlSi_2O_6)$
^{M}: Minor phase

Table 5. Characterisation data of the glazes obtained from the different tested frits.

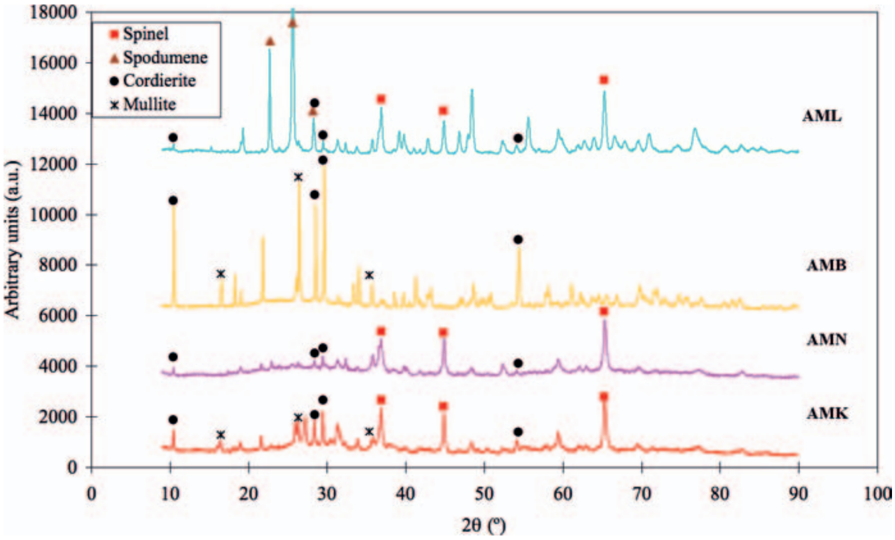

Figure 8. Diffractograms of the glazes obtained from the frits prepared with different types of fluxes

6. GLAZES OBTAINED FROM THE NEW FRIT COMPOSITION (AMB)

With a view to obtaining glazes from frit composition AMB, with appropriate characteristics and free of defects when fired at 1180°C, glaze compositions were prepared with this frit and other raw materials: nepheline and spodumene. First, the addition of 10% by weight of these raw materials to frit AMB was tested separately. Table 6 sets out the characterisation data. It can be observed that using nepheline gives rise to glazes with low transparency, possibly due to the appearance of sapphirine, a crystalline phase that has a high refractive index (170-1.73) compared with that of the other phases. Using spodumene favours cordierite formation, as the corresponding diffractogram (Figure 9) shows, and yields a highly transparent matt glaze. However, since cordierite has a low coefficient of expansion, the resulting glaze tended to exhibit flaking at the edge of the piece obtained in the laboratory.

	AMB-N	AMB-E
RAW MATERIAL	**Nepheline**	**Spodumene**
L*	88.0	81.1
a*	0.08	0.52
b*	1.87	6.82
TP	0.65	0.81
Gloss 60°	9	4
Crystalline phases	Cordierite Sapphirine Mullite	Cordierite Mullite Akermanite^{M}

Akermanite: $Ca_2Mg(Si_2O_7)$, Cordierite: $Mg_2Al_4Si_5O_{18}$, Mullite: $Al_6Si_3O_{15}$, Sapphirine: $(Mg,Al)_8(Al,Si)_6O_{20}$
^{M}: Minor phase

Table 6. Characterisation data of the glazes obtained from frit AMB and other crystalline raw materials.

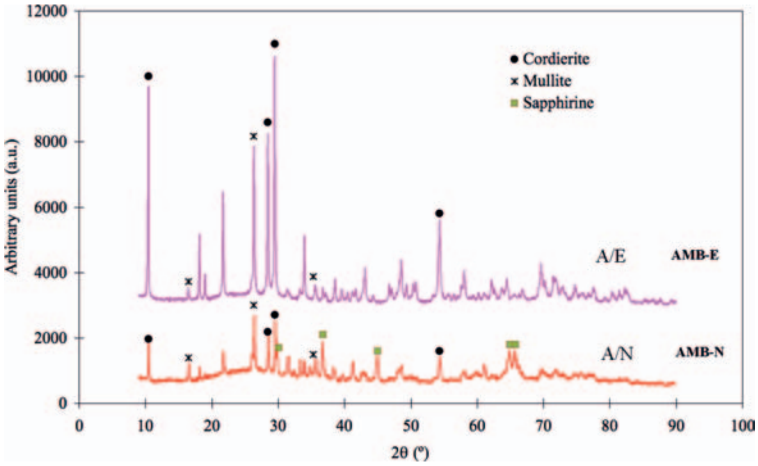

Figure 9. Diffractograms of the glazes prepared using frit AMB and nepheline or spodumene as raw materials.

Since glaze AMB-E was the one that gave rise to greater transparency, the composition was optimised by performing design of experiments (DOE). In this DOE, the raw materials used in glaze preparation were taken as variables (frit, spodumene and kaolin) and transparency, mattness and glaze-body fit were optimised. From the result of the DOE, a glaze composition, designated AMB-E*, was obtained with the characteristics detailed in Table 7. These indicate that this composition produces a transparent matt glaze, in which the crystalline phase causing the matt appearance is cordierite, as the diffractogram in Figure 10 shows.

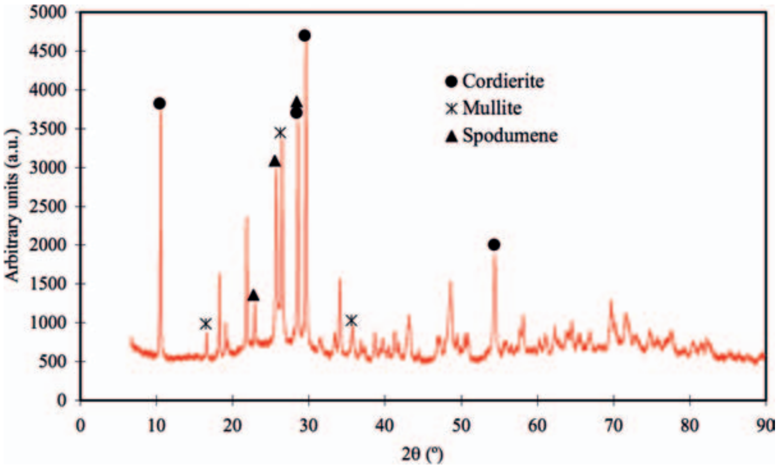

Figure 10. Diffractogram of glaze AMB-E. 1180°C*

	AMB-E*
L*	82.11
a*	0.64
b*	4.07
TP	0.81
Glaze 60º	4
Crystalline phases	Cordierite: $Mg_2Al_4Si_5O_{18}$ Mullite: $Al_6Si_3O_{15}$ Spodumene: $LiAlSi_2O_6$ Akermanite^M: $Ca_2Mg(Si_2O_7)$

^{M}: *Minor phase*

Table 7. Characterisation data of the optimised glaze composition

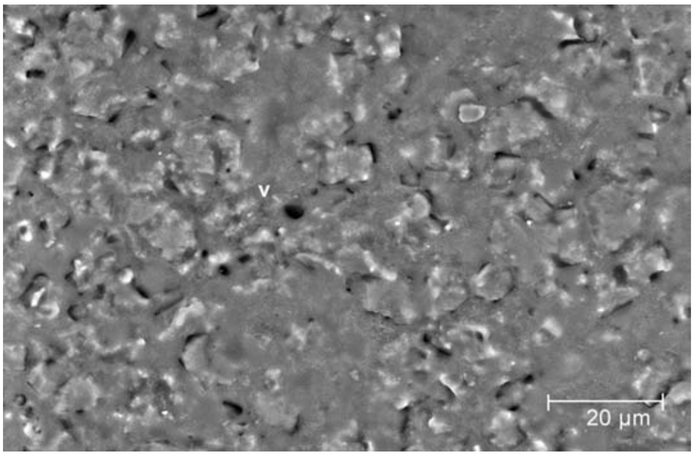

Figure 11. Surface of the piece obtained with glaze AMB-E.*

Figure 11 displays the surface of the glaze, which evidences the existence of a great number of crystals of considerable size embedded in the glassy phase (V). Observation of the cross-section of these glazes (Figures 12 and 13) shows that they are made up of glassy phase and two types of crystalline phases: larger-sized cordierite crystals, marked C, and smaller-sized mullite crystals, marked M, in Figure 13.

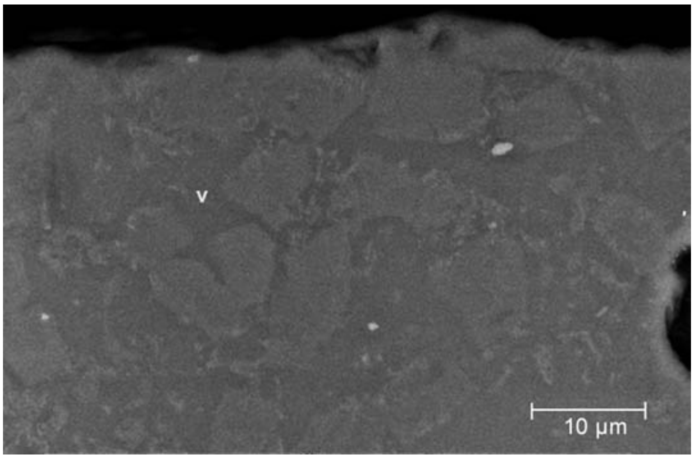

Figure 12. Cross-section of glaze AMB-E.*

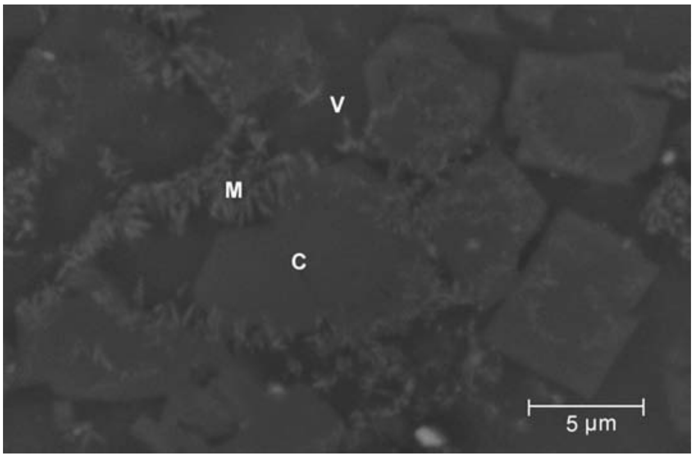

Figure 13. Cross-section of glaze AMB-E.*

The results of the determination of the chemical resistance to high-concentration acids and alkalis (Table 8) indicate that the glaze undergoes no appreciable deterioration with any of the tested agents.

Reagents	Classification according to the standard
Hydrochloric acid 18%	GHA
Lactic acid 5%	GHA
Potassium hydroxide 100 g/l	GHA

Table 8. Chemical resistance of glaze AMB-E.*

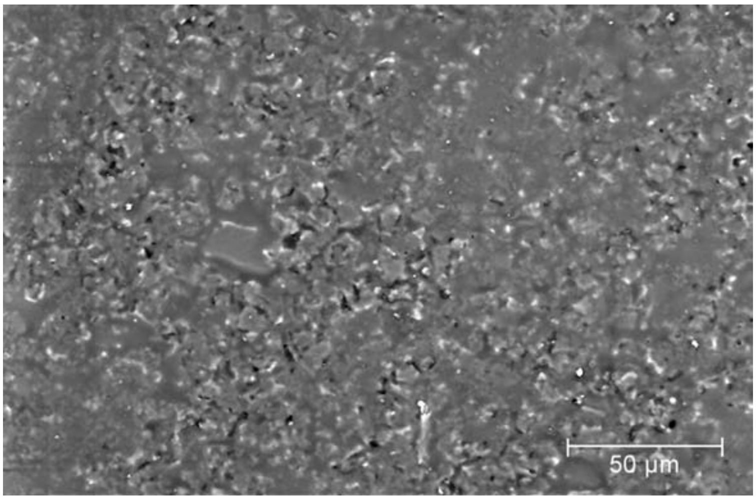

Figure 14. Surface of piece AMB-E attacked with HCl*

Figures 14-16 show photographs of test specimen surfaces that have been subjected to attack. They evidence the small magnitude of the attack, since there only appears to be a slight dissolution of the glassy phase, while the cordierite crystals have not been attacked by any of the tested agents.

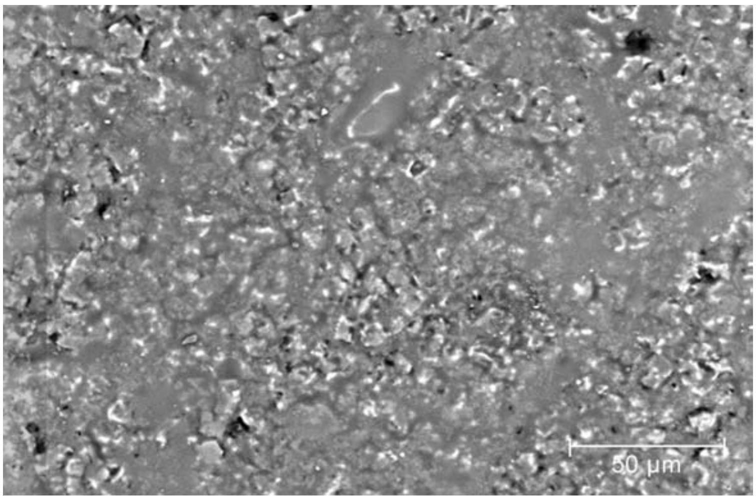

Figure 15. Surface of piece AMB-E attacked with lactic acid*

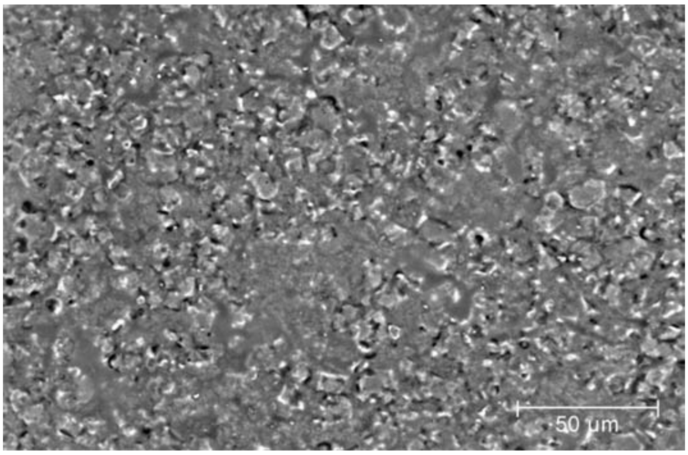

Figure 16. Surface of piece AMB-E attacked with KOH*

As already indicated previously, cordierite is a phase that has a low coefficient of expansion; glazes with a high quantity of this phase, as is the case of AMB-E*, could tend to have flaking problems. However, the glaze obtained in this study displays appropriate glaze-body fit, and yields pieces without this defect.

7. CONCLUSIONS

The matt calcium starting glaze studied owes its transparent matt appearance to anorthite, a crystalline phase that forms during firing due to the reaction of different glaze components during heat treatment. The presence of anorthite in the glaze surface is the cause of the deterioration that this glaze undergoes when it is subjected to the standard chemical resistance test using strong acids.

A transparent matt glaze with improved chemical resistance has been obtained from a frit with high magnesium oxide content. The appearance of this glaze is determined by the presence of the cordierite crystalline phase, whose low refractive index and large-sized crystals give rise to a glaze with high transparency.

The formation of cordierite from a frit with the appropriate composition (high alumina and magnesium oxide content, and absence of calcium oxide) is favoured when boric oxide is used as a fluxing oxide. In addition, the use of spodumene instead of nepheline as a raw material in the glaze composition also favours cordierite formation in the glaze.

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