

VITRIFICATION STUDIES ON PORCELAIN TILE COMPOSITIONS WITH SPANISH RAW MATERIALS AND NEW FLUXES

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ABSTRACT

This paper describes the fluxing action of three raw materials, namely talc, nepheline syenite and lithium feldspar, when used partly to replace potassium feldspar as flux in a porcelain tile composition. Formulations were prepared with several clays and two different contents – 5% and 10% - to partly replace the potassium feldspar. The presence of talc and lithium feldspar produced a less viscous glassy phase, which allowed a lower sintering temperature, obtaining water absorption rates below 0.5% at relatively low temperatures. For this reason, the use of 10% talc leads to a significant reduction in the dimensional stability range compared with the firing temperature.

1. INTRODUCTION

The increasing growth in the production of porcelain floor tiles (both glazed and unglazed), as well as a rise in the costs related to importing foreign raw materials and to the high firing temperatures required to manufacture products with good technical qualities (with water absorption rates of less than 0.5%) has two main implications for the Spanish ceramics sector – on the one hand, a loss of competitiveness compared with countries producing or close to the source of such raw materials and on the other hand, increased porcelain tile production costs.

Porcelain tile production using foreign raw materials (mainly Ukrainian clay and Turkish feldspars) increased significantly in the Spanish province of Castellón in the years 2006 and 2007. Figures shows that in 2007, over three million tonnes of clay and feldspars were imported through the port of Castellón, of which 71% of the clay was from the Ukraine and 81% of the feldspars came from Turkey [1,2].

On the other hand, according to ASCER, in 2006, Spain produced more than 113 million square metres of porcelain tiles (compared to 94 million sq. metres in 2005), of which over 92% was glazed porcelain tile and only 13% were 'technical' or unglazed porcelain tiles.

This high level of glazed porcelain tile production enables raw materials with fewer restrictions regarding the content of chromophore elements such as iron or titanium to be used, so that the use of Spanish raw materials (clays) is a viable alternative.

With regard to the fluxes included in these compositions, it is common practice in the Castellón ceramics industry to use potassium feldspars or sodium-potassium feldspars mixtures as a way of introducing such oxides. As with clay, these compounds need to have low levels of colour-generating impurities as well as high concentrations of fluxing oxides (alkali elements such as sodium and potassium).

In order to understand the effect on sintering produced by adding different types of fluxes, this paper selected three different fluxes – namely, nepheline syenite, lithium feldspar and talc – to formulate compositions based on several Spanish clays.

The main sintering mechanism that takes place during the firing of porcelain tiles is during the liquid phase when the most fusible compounds melt. This degree of sintering is closely linked to the size of the particles in the sample [3,4], especially when working with eutectic compositions, because in order for fusion to take place at a eutectic temperature, the largest possible number of contact points need to exist between the different particles in the mixture. Therefore, particle size was carefully controlled in this study of sintering from the point of view of the composition to eliminate the effect of a 'particle size' variable.

2. EXPERIMENTAL PROCEDURE: RAW MATERIALS AND METHODOLOGY

To perform the experiments performed in this study, three types of Spanish clay were used: an illitic-kaolinitic clay from the Ariño mining region in the province of Teruel, supplied by the company Euroarce S.A., referenced SG-752 STD; another one from the Crivillén area referenced CAV; and a third clay from the Ciudad-Real region, referenced CR (the latter two were both supplied by Sabater Mining). All three clays are commonly used nowadays by the Spanish tile manufacturing sector to formulate porcelain tile and stoneware tile compositions.

The raw materials used as fluxes were a lithium feldspar (FLi), nepheline syenite (Ne-Si) (both supplied by C.F.M Minerales S.A.), a Spanish-sourced potassium feldspar (FV-016) (supplied by Euroarce S.A) and talc (supplied by Quimialmel S.A.).

With the aim of improving whiteness, the clays used in this study were dispersed and screened through 150µm mesh [5]. Table I shows the chemical composition of the resulting clays, obtained with an XRF spectrometer in combination with the chemical analysis provided by the various suppliers of the fluxes.

	SG-752 STD	CAV clay	CR clay	FV-016	FLi	Ne-Si	Talc
SiO ₂	67.50	65.6	56.3	<70.00	64.20	55.80	58.90
Al ₂ O ₃	20.20	19.8	27.1	>16.50	17.12	24.40	0.20
Fe ₂ O ₃	2.19	2.48	2.07	<0.15	0.08	0.10	0.30
CaO	0.28	0.33	0.14	0.20-0.80	-	1.00	2.50
MgO	0.29	0.44	0.27	-	-	0.05	30.00
Na ₂ O	0.08	0.16	0.96	2.00-3.00	0.87	7.80	0.06
K ₂ O	1.51	2.24	3.31	>10.30	0.23	9.00	<0.01
TiO ₂	1.11	1.08	1.22	0.05	-	0.06	<0.10
Li ₂ O	-			-	7.40	-	-
MnO	0.01			-	-	-	-
P ₂ O ₅	0.08			-	-	-	-
PPC	6.72	6.73	6.11	-	0.92	0.50	6.00

Table I. Chemical analysis (% by weight) of the raw materials used in this study. The chemical analysis of the fluxes was provided by the suppliers of these materials.

Once these clays had been screened, different porcelain tile compositions were formulated (table II) with the fluxes characterised in table I. It should be noted that these preparations were based on two compositions used in a previous study [5], referenced P9 and P10, whose objective was to introduce fluxes that are not commonly used in the ceramic industry.

To create test pieces of the various compositions, the raw material mixtures were first ground in a lab planetary ball mills to a residue of less than 1% by weight at 63 μ m. The resulting suspension was analysed with a laser diffraction unit (Beckman Coulter LS) and then dried in a lab oven at 110°C for 24h. After drying, the mixture was ground in planetary ball mills for 5 minutes to break up the aggregates. Finally, the composition was moistened to 6% on a dry basis and uniaxially pressed at a pressure of 350kg/cm² in a Nannetti lab press with a 5 cm diameter die.

	SG-752 STD	CAV clay	CR clay	FV-016	Ne-Si	FLi	Talc	Quartz
P9	25		25	30				20
P10		50		30				20
P100		50		20	10			20
P101		50		20		10		20
P102		50		20			10	20
P106	25		25	20	10			20
P107	25		25	20		10		20
P108	25		25	20			10	20
P109		50		25	5			20
P110		50		25		5		20
P111		50		25			5	20
P112	25		25	25	5			20
P113	25		25	25		5		20
P114	25		25	25			5	20

Table II. Load formulae of the compositions under study and of the two reference compositions. (% by weight).

The test pieces of the various compositions thus obtained were fired at different maximum temperatures according to the following cycle:

- From ambient temperature to 600°C at 10°C/min, with a 5-minute dwell at maximum temperature.
- From 600°C to T_{max} at 10°C/min, with a 5-minute dwell at maximum temperature.

Different parameters were then measured on each of them, including water absorption, linear firing shrinkage, fired bulk density, microstructure characterisation and analysis (using scanning electron microscopy with an SEM/EDX LEO-44-I unit fitted with an Oxford ISIS energy-dispersive X-ray analysis instrument) and an X-ray diffraction unit (SIEMENS D500 diffractometer with a copper cathode, nickel filter and scintillation detector, using the random powder sample distribution method).

3. RESULTS AND DISCUSSION

At this point, given that the results using the various clays were all fairly similar, and that the most significant results were obtained when 10% contents of the new fluxes were used, this section only analyses the samples formulated with CAV clay in which 10% of the FV-016 feldspar was replaced with the new fluxes (P100-P101-P102).

Table III presents the statistical indicators relating to particle size distribution in the samples analysed by laser diffraction (in percentiles).

	d10	d50	d90
P10	1.20	6.78	23.52
P100	1.25	5.96	19.18
P101	1.18	6.67	22.46
P102	1.52	8.89	32.85

Table III. Percentiles of the samples studied (% by volume) using the Fraunhofer theory.

The vitrification chart for the compositions formulated with CAV clay and 10% flux are shown in figure 1. The same figure also displays the water absorption and linear shrinkage values obtained at the time for composition P10. In turn, figure 3 shows bulk density for the fired pieces versus temperature.

Analysis of Figures 1, 2, and 3 allows several conclusions to be drawn:

- By adding 10% of either talc or lithium feldspar to replace 10% of the potassium feldspar (the range varies from 30% in the P10 composition to 20% in the new ones), greater sintering is produced at relatively low temperatures, given that linear firing shrinkage at 1150°C increases from 6.9% in the original P10 sample to 7.7 and 8.7% in the lithium feldspar and talc compositions respectively. This effect can also be seen in the water absorption values, as at the same temperature, these values go down dramatically to a level below 0.5% when any of these fluxes is used.
- Maximum densification (fired bulk density) for the samples with 10% talc and lithium feldspar is obtained at a temperature slightly below 1170°C, whereas for the samples with 10% nepheline syenite, the temperature rises to values around 1210°C. These temperatures match the maximum linear firing shrinkage observed in figure 1.
- When 10% talc is used, the dimensional stability range is very limited, possibly as a result of low viscosity in the molten phase [6]. In contrast, the use of lithium feldspar is seen not to have such as 'aggressive' effect as talc and allows a dimensional stability range that can even be considered

as suitable. The use of 5% talc increases dimensional stability in the piece compared with the range obtained for the piece with 10% talc (figure 2).

- With regard to the use of 10% Ne-Si, sintering in the test pieces is seen to be lower until a temperature range of around 1180°C is reached, whereupon it presents a higher fired bulk density and lower water absorption.

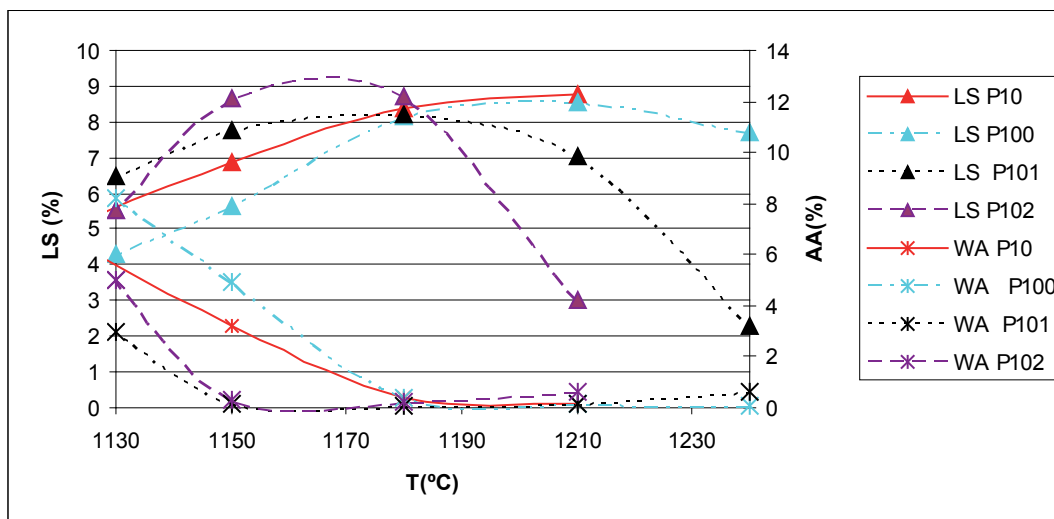


Figure 1. Vitrification diagram for the various fluxes at 10% by weight.

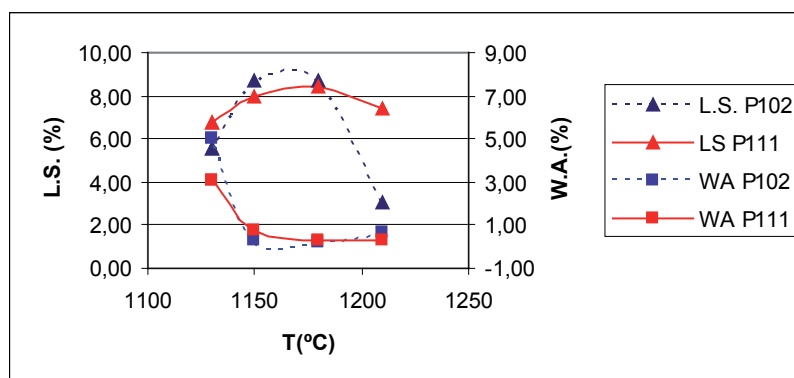


Figure 2. Vitrification diagram for samples P102 and P111 (10 and 5% talc respectively).

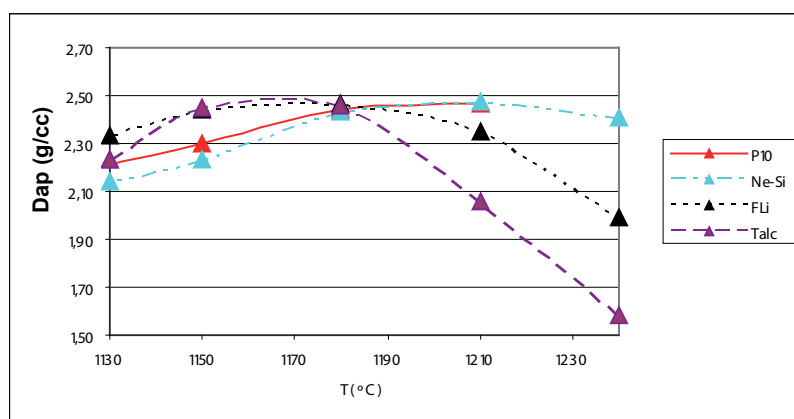


Figure 3. Comparison of fired bulk density values between the reference sample (P10) and the samples formulated with CAV clay and 10% by weight of the new fluxes.

Figure 4 shows the SEM micrographs for the samples: 4a, with nepheline syenite formulations at 1180°C; 4b, with lithium feldspar at 1150°C; and 4c, talc at 1150°C (samples with water absorption of less than 0.5%).

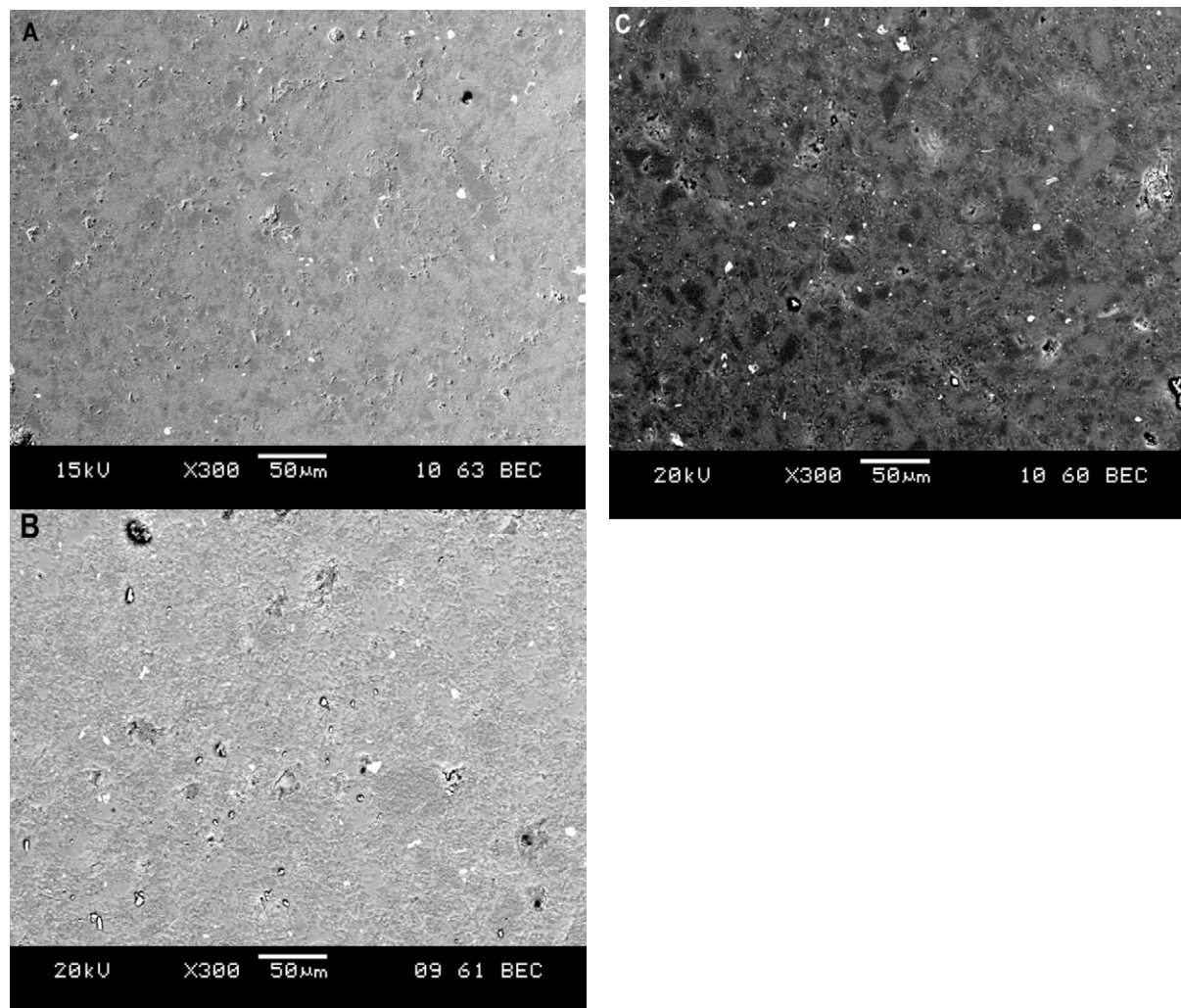


Figure 4. Micrographs of samples a) P100 b) P101 c) P102 on samples with water absorption below 0.5%, obtained with back-scattered electrons.

The micrograph corresponding to the nepheline syenite sample fired at 1180°C (figure 4a) reveals the presence of unmelted quartz particles (dark shadows), some of which still have an irregular morphology, just like the potassium feldspar particles. The presence of such a type of particle is due to the short period of time (5 minutes) the sample was held at maximum firing temperature. Despite such a short residence time at maximum temperature, the presence of closed porosity can be observed (more or less round pores) made up of a large number of small-size pores (smaller than 10µm), due to the fact that the pressure of the gas inside the pores produced by the decomposition of volatile elements in the feldspar particles is still not very high [3,7,8,9]. By using energy-dispersive X-ray spectroscopy (EDX) in this same micrograph, areas with an alumina:silica ratio of nearly 2:1 were detected, which indicates the presence of irregularly-shaped

mullite, corresponding to primary mullite [10].

For its part, in the micrograph corresponding to the lithium feldspar sample fired at 1150°C (Figure 4b), the presence of a larger-sized ($>10\mu\text{m}$) closed porosity can be observed, due probably to lower viscosity in the molten phase [11], which provides lesser resistance to pore expansion.

Finally, in the micrograph in figure 4c, it can be seen that when magnesium is used, a low viscosity molten phase is generated which produces rapid expansion of the gases trapped inside the closed pores. This creates a closed porosity with large-size pores. With regard to quartz particles, due to the short residence time that the sample was held at the maximum firing temperature of 1150°C, irregularly-shaped particles were observed to remain. The same thing occurred when lithium feldspar was used, where, due to the low viscosity in the molten phase, the quartz particles dissolved more quickly to become somewhat more spherical in shape than when nepheline syenite was used.

When studying the results of the XRD analysis of those phases in which scanning electron microscopy was performed on the same samples (figure 5), although the presence of mullite had not been detected by the SEM, the XRD tests show that it is in fact present, even at these relatively low temperatures and short residence times at maximum firing temperature.

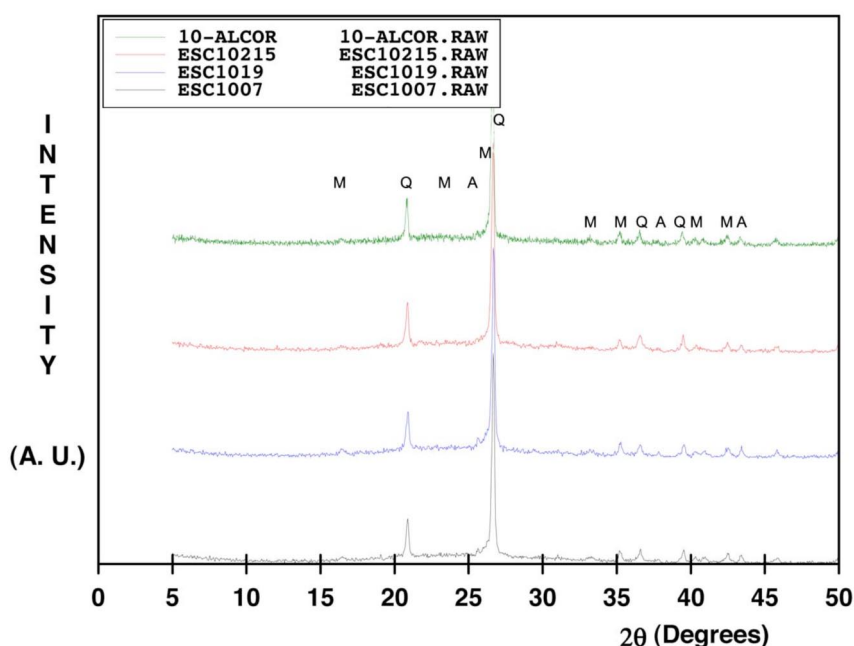


Figure 5. XRD of the same samples as those in the micrographs. From the bottom upwards: P100-P101-P102-P10. The presence of mullite (M), quartz (Q), and alumina (A) can be seen.

This type of mullite is probably primary mullite, although the possibility of these crystals growing into needle-like shapes (type III mullite) cannot be ruled out, as according to the literature consulted [5,12,13], the presence of a low-viscosity molten phase would tend to enhance the growth of secondary mullite in the quartz-feldspar contact areas.

4. CONCLUSIONS

This paper shows how the addition of fluxes such as lithium feldspar or talc can help to reduce melting temperatures in porcelain tile compositions. Adding these substances generates a glassy phase with lower viscosity, where the remaining particles such as quartz can dissolve more quickly.

The generation of a low-viscosity glassy phase can create problems, on the one hand, due to the size of the pores constituting the closed porosity, a characteristic which needs to be taken into account in the production of unglazed porcelain tiles, and on the other hand, problems of low dimensional stability in fired tiles (such as when 10% talc is used in the composition).

XRD analysis shows the formation of a mullite phase even at relatively low temperatures and short residence times. This mullite could be considered to be secondary mullite (type III) as the growth of needle-shaped crystals may be enhanced by the low viscosity of the molten phase. This last issue has not yet been verified by SEM analysis.

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