EFFECT OF ZINC OXIDE GRANULE SIZE ON MELT BEHAVIOUR IN FRITTING

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1. INTRODUCTION

Ceramic frits are the major ceramic wall tile glaze component. With the implementation of the single-fire wall tile manufacturing process, zinc oxide has achieved great importance as a raw material in the frits used for making wall tile glazes by acting as a high-temperature flux [1] and contributing required glaze properties, such as surface sealing after carbonate decomposition in the tile body and low viscosity at firing temperature. The zinc oxide content in these frits usually ranges from 8 to 12% by weight, and zinc oxide is considered one of the main frit constituents [2].

Zinc oxide is usually supplied as a powder with a very fine particle size 1 µm with agglomerates up to 40 µm). The fine size encourages its incorporation into the arising glassy phase during raw materials fusion in frit production, and lowers melt viscosity, thus enabling the more refractory raw materials (quartz, alumina and zirconium silicate) to dissolve more readily. However, the small particle size makes these particulates exhibit a strong tendency to pack together, giving rise to low flowability, which hinders all the processes in which this material needs to be handled, such as charging and discharging silos and hoppers, mixing, conveying, etc. [3] The small particle size also encourages particulates being drawn along by air streams, zinc oxide typically being found amongst the exhaust products collected in fritting kiln stacks.

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[1] Escardino, A. *Single-fired ceramic wall tile manufacture.* In: II World Congress on Ceramic Tile Quality. QUALICER. 1992, p. 111-140.

[2] Amorós, J.L. *Glazes for floor and wall tiles. Evolution and perspectives.* In: II World Congress on Ceramic Tile Quality. QUALICER, 1992, p. 73-103.

[3] Sánchez, E.; Enrique, J.E. *Materias primas empleadas en la elaboración de fritas cerámicas.* In: I Jornadas sobre materias primas de la industria cerámica. Castellón: Asociación Española de Técnicos Cerámicos, 1996.

To avoid the problems associated with using zinc oxide powder, granulated zinc oxide, made by compacting the fine powder, can be employed. Zinc oxide flowability improves when the material is granulated. However, zinc oxide granules are likely to be incorporated into the glassy phase less readily than the fine powder [4,5].

2. OBJECTIVE AND SCOPE

The present study was conducted with a view to determining the changes that occur in the frit production process on using granulated instead of finely powdered zinc oxide. The study was programmed in two stages. The first stage, conducted on a laboratory scale, was performed with various samples of zinc oxide with different granule size distributions, in order to attempt to establish which granule size could be used without producing important alterations in the frit production process. The second stage, performed on an industrial scale, was designed to verify the laboratory findings, and thus allow benefiting from the full advantages in handling, conveying, mixing and working conditions.

3. LABORATORY RESEARCH

3.1.- MATERIALS AND EXPERIMENTAL PROCEDURE

3.1.1.- Materials

To carry out the study, a zinc oxide (sample R) of the type commonly used in making ceramic frits was used as reference material. It had a ZnO purity of 99.5% and exhibited the particle size distribution shown in figure 1, obtained by laser-light diffraction using the wet method.

The other raw materials used were granulated zinc oxides made industrially from zinc oxide R, with different agglomerate size distributions. The agglomerate size range and mean agglomerate diameter (D_{50}) of each granulated zinc oxide sample, below which 50% by weight of the agglomerates was found, were as follows:

- M: Agglomerates sized smaller than 700 μm. D_{50}=200 μm
- A: Agglomerates sized smaller than 200 μm. D_{50}=125 μm
- B: Agglomerates sized between 200 and 700 μm. D_{50}=350 μm
- C: Agglomerates sized larger than 700 μm. D_{50}=1100 μm
- D: Agglomerates sized between 700 and 1200 μm. D_{50}=780 μm
- E: Agglomerates sized between 1200 and 2000 μm. D_{50}=1750 μm

Figure 2 presents the agglomerate size distributions found by dry sieving these materials.

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[4] Taylor, J.R.; Bull, A.C. *Ceramics glaze technology.* Oxford: Pergamon Press, 1986.

[5] Tooley Fay V. *The handbook of glass manufacture.* 3rd ed. New York: Ashlee Publishing, 1984.

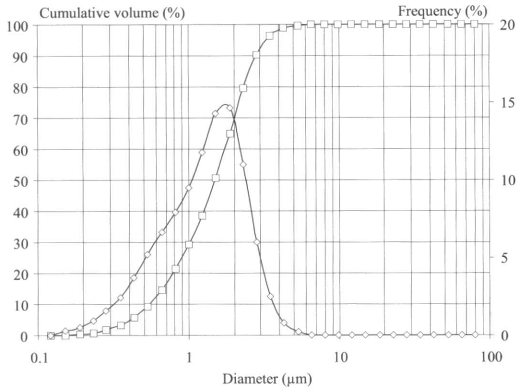

Figure 1. *Particle size distribution of the reference zinc*

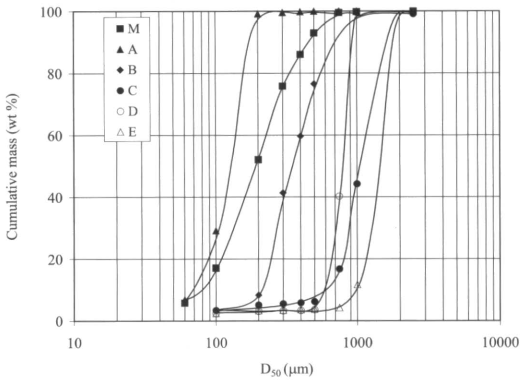

Figure 2. *Agglomerate size distribution of the tested zinc oxides.*

A frit composition (F) of the type commonly used to produce opaque white glazes for single-fired wall tile was also prepared. The composition was made up of the usual materials employed in the industrial production of this type of frit, in the proportions listed in table 1.

Raw materials	wt%
Zinc oxide	10.9
Potassium feldspar	18.5
Quartz	33.9
Calcium carbonate	7.9
Dolomite	8.8
Colemanite	9.3
Potassium nitrate	1.0
Zirconium silicate	9.7

Table 1. *Frit F batch formula.*

3.1.2.- Experimental procedure

3.1.2.1.- Making the frits

Each zinc oxide sample was used to prepare a frit, whose batch formula is given in table 1. This yielded seven frits, which were given the reference F followed by the zinc oxide reference. The procedure used for making the frits is described below.

The raw materials used to make the frits were homogenised in a fast laboratory mill without any milling elements. The resulting powder was fused in alumina crucibles in an electric laboratory kiln, according to the following heat-treatment cycle:

- Fast rise to 500ºC.
- Heating at a rate of 20ºC/min from 500ºC to a peak temperature of 1600ºC.
- 30-min dwell at peak temperature.

After the residence time at peak temperature, the melt was quenched in cold water to produce the actual frit.

3.1.2.2.- Making the glazes

A glaze suspension was made up with each frit by milling the respective mixtures in a fast laboratory alumina ball mill. The mixtures consisted of 92% frit, 8% kaolin, 0.2% sodium tripolyphosphate (relative to the solid) and 0.2% sodium carboxymethylcellulose (relative to the solid), together with the amount of water required to obtain a 70% solids content (all percentages are by weight). The mixtures were milled until a reject of about 1 wt% was reached on a 40-μm mesh screen.

The resulting glaze suspensions were applied with a variable-speed automatic applicator to a green engobed body of the type used in single-fire wall tile manufacture. The applied glaze coating was about 400-μm thick. The glazed specimens were dried in an electric laboratory oven at 110°C and then fired in an electric laboratory kiln, ramping at 25°C/min with a 6-min dwell at peak firing temperature. The following different peak firing temperatures were tested: 1060, 1080, 1100 and 1120°C.

The colour of the fired glaze coatings was determined on a spectrophotometer by means of the CIELab system, using a C illuminant and CIE 2° observer. The following parameters were used to compare the glaze colours:

- Chromatic coordinates: L* (L*=0 black, L*=100 white), a* (a*<0 greenness, a*>0 redness), b* (b*<0 blueness, b*>0 yellowness)
- Whiteness index: Wi(HUNTER [60])
- Yellowness index: Yi (ASTM D1925)

Glaze surface gloss was determined on a reflectometer, measuring at an angle of 20°.

3.1.2.3.- Identification of crystalline structures

The crystalline structures were identified by X-ray diffraction (XRD) of the powdered sample. The mineralogical species appearing in the resulting diffractograms were identified by means of the JCPDS files for pure crystalline phases.

3.1.2.4.- Observation of the samples by scanning electron microscopy (SEM)

The samples were studied and analysed with a scanning electron microscope hooked up to an energy-dispersive X-ray analysis (EDXA) instrument.

3.2.- RESULTS

3.2.1.- Influence of zinc oxide granule size on frit and resulting glaze properties

3.2.1.1.- Frit properties

Seven frits were made, using a different zinc oxide for each. It was observed during frit preparation that the zinc oxide samples with the largest aggregate sizes gave rise to foaming in the crucible.

The appearance of foam is usually due to the incomplete removal of the gases contained in the melt and is normally associated with a deficient fusion process [4,6], which impedes complete fusion of the most refractory raw materials (quartz and zirconium silicate). To establish whether this was the case, XRD was run on frits FR and FC to determine if they contained any crystalline structures. The results showed no peaks that could be associated with crystalline phases in either frit, while the diffractograms exhibited the typical shape of materials of a vitreous nature such as frits. That is, there were no significant amounts of unmelted materials, though there might be minor quantities below the instrument's detection limit (1%).

As certain unmelted inclusions (quartz) tend to float in the molten glassy phase, XRD was carried out on the foam that arose in the crucible on fusing the sample with zinc oxide C. The diffractogram exhibited cristobalite peaks. The cristobalite came from unmelted quartz that converted to cristobalite at high temperatures (over 1470ºC).

The foregoing suggests that using large zinc oxide granulates favours foam formation and the appearance of unmelted quartz inclusions, probably owing to a very viscous glassy phase at fusion temperature hindering outgassing and the dissolution of the most refractory raw materials. This high viscosity was in turn likely to be the result of the retarded dissolution or fusion of the granulated zinc oxide. This delay in zinc oxide incorporation into the glassy phase would shift the optimum fusion range to higher temperatures.

3.2.1.2.- Properties of the glazes made from the frits

The frits were used to prepare the respective glaze compositions, which were applied to the porous bodies and fired at different peak firing temperatures. Table 2 presents the colour and gloss determination data of the glazes obtained at 1100ºC.

Frit	L*	a*	b*	Wi	Yi	R(‰)
FR	93.9	-0.3	2.5	84.6	4.8	75
FM	94.0	-0.3	2.4	84.9	4.7	75
FA	93.9	-0.3	2.6	84.5	5.0	77
FB	94.2	-0.4	2.3	85.5	4.5	71
FC	93.9	-0.4	2.5	84.5	4.9	67
FD	94.3	-0.4	2.4	85.4	4.6	68
FE	94.9	-0.4	2.6	84.2	5.1	66

Table 2. *Chromatic coordinates and whiteness and yellowness indices of the glazes obtained at 1100ºC with the frits made with the studied zinc oxides.*

It can be observed that glaze colour remained steady regardless of the zinc oxide used in the frits employed in the glaze compositions. However, the glazes did exhibit differences in gloss. The data show that gloss decreased as zinc oxide granule size rose.

This effect can be observed on plotting glaze gloss versus granulated zinc oxide sample mean diameter (D_{50}) (figure 3).

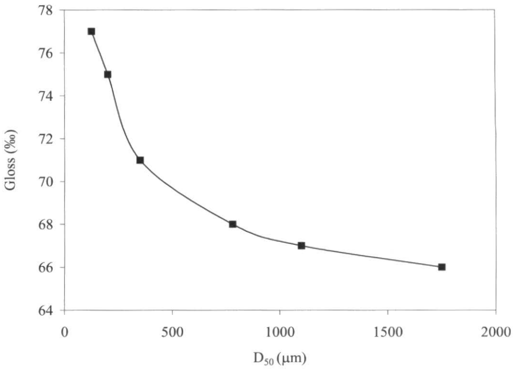

Figure 3. *Variation of gloss with the mean zinc oxide agglomerate size used in the frits contained in the glazes obtained at 1100ºC.*

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[4] Taylor, J.R.; Bull, A.C. *Ceramics glaze technology.* Oxford: Pergamon Press, 1986.
[6] Fernández, J.Mª. *El vidrio.* 2ª ed. Madrid: CSIC, 1991.

This relationship between glaze gloss and zinc oxide agglomerate size could be due to the presence of quartz or cristobalite particles in the frit, as the presence of crystalline particles in frits and glazes lowers gloss.

3.2.2.- Influence of zinc oxide granule size on the fusion process

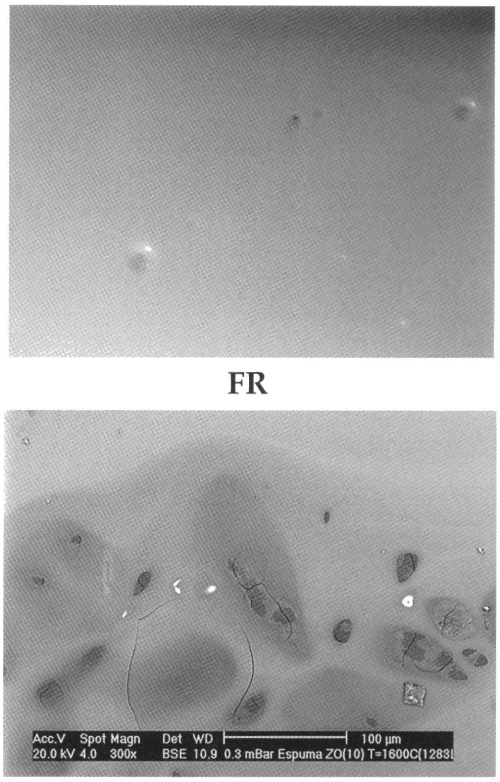
3.2.2.1.- Amount of arising foam

The test that follows was conducted to quantify the amount of foam that formed during the fusion process.

The raw materials mixture was fused in an electric laboratory kiln as described in point 3.1.2.1. After the set residence time at peak temperature, the crucible with the melt was withdrawn from the kiln and allowed to cool to room temperature instead of quenching the melt in water to produce the frit. The surface of the melt was then examined with an optical microscope. Figure 4 presents the photographs corresponding to samples FR and FC. The bubbles that caused foaming can be observed at the melt surface. Sample FR, which produced no foam, contained few bubbles, whereas sample FC, which did produce foam, exhibited a considerably larger number of bubbles.

Image analysis was used to determine the area occupied by bubbles. Table 3 lists the resulting data. Frits FR, FM and FA caused no foaming and the area occupied by bubbles was less than 1%. The other samples encouraged foam formation and the area taken up by bubbles was over 1%.

With a view to establishing whether there was any relationship between agglomerate size and the tendency to produce foam, the area occupied by bubbles was plotted versus the mean zinc oxide agglomerate size used (figure 5).



FR

FC

Figure 4. *Photographs of the surface of the crucibles containing samples fused at 1600°C.*

Frit	% area occupied by bubbles
FR	0.40
FM	0.75
FA	0.80
FB	8.24
FC	3.59
FD	6.98
FE	1.60

Table 3. *Proportion of bubbles present at the melt surface.*

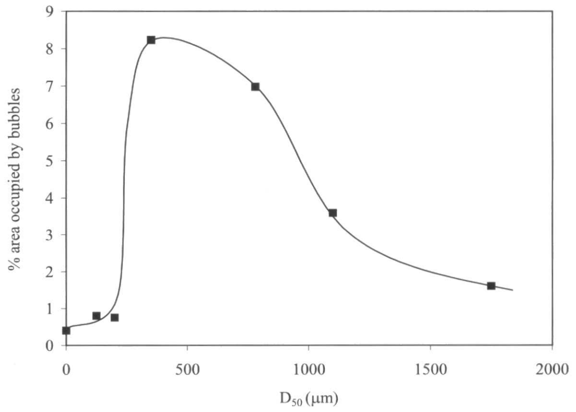


Figure 5. *Variation of the bubble-occupied area with mean zinc oxide agglomerate size.*

The figure shows the effect mentioned above. Sample FR, FM and FA behaviour is practically identical and no foam forms. In the other samples, which all tended to produce foam, increasing granule size lowered the quantity of bubbles found at the melt surface. This fact could be due to retarded fusion caused by using large-size zinc oxide granules and to the outgassing mechanism.

The bubbles in the melt come from air between the particles of the raw materials mixture and from the gases that evolve with the breakdown of certain raw materials (calcium carbonate, dolomite, colemanite and potassium nitrate in this case) during heat treatment. Outgassing takes place by bubbles travelling upwards to the surface of the melt, where the bubbles burst and disappear. According to Levich [6], the rate at which bubbles rise in a melt obeys the following relation:

$$v = \frac{1}{3} \cdot r^2 \cdot g \cdot \frac{(\rho_l - \rho)}{\eta}$$

where v represents bubble velocity of rise; r bubble radius; ρ_l-ρ the difference between melt density and gas density in the bubble, and η melt viscosity.

Any variation in the viscosity of the melt will modify bubble rate of rise and hence its removability. Thus the lower the viscosity of the melt, the more readily will the bubbles be cleared.

The inference is hence warranted, that if the fusion process is retarded by using zinc oxides with a larger granule size, the differences found with regard to the quantity of bubbles occurring at the melt surface can only be due to different melt viscosities at fusion temperature (1600°C). In other words, bubble outgassing is at a different stage in each sample. The findings can therefore be satisfactorily explained by assuming that the samples with the larger-size zinc oxide granules produce more viscous melts, i.e., samples FR, FM and FA will already have removed the bubbles, sample FB will be eliminating the bubbles, and the other samples will be initiating this process.

3.2.2.2.- Settling of zinc oxide granules in the melt

The crucibles containing the mixtures fused at 1600°C, obtained as described in the foregoing section, were cross-sectionally sliced. The samples made with large zinc oxide granule sizes (FC, FD and FE) exhibited a green-coloured region in the glass at the bottom of the crucible (figure 6). EDXA runs were performed on two regions with a different appearance in the FC sample. One run was made in a white region and another in the green region at the bottom of the crucible. The results are shown in figure 7.

Comparison of these analyses revealed that the green region at the bottom of the crucible was made up of the same elements as the rest of the glassy mass (white region). The difference lay in the much greater zinc content, i.e., a zinc-rich glassy phase was involved.

These outcomes suggest that the largest zinc oxide granules settle during the fusion process, producing a glassy phase rich in zinc oxide at the bottom of the crucible. This phenomenon obviously becomes more important as starting zinc oxide granule size increases.

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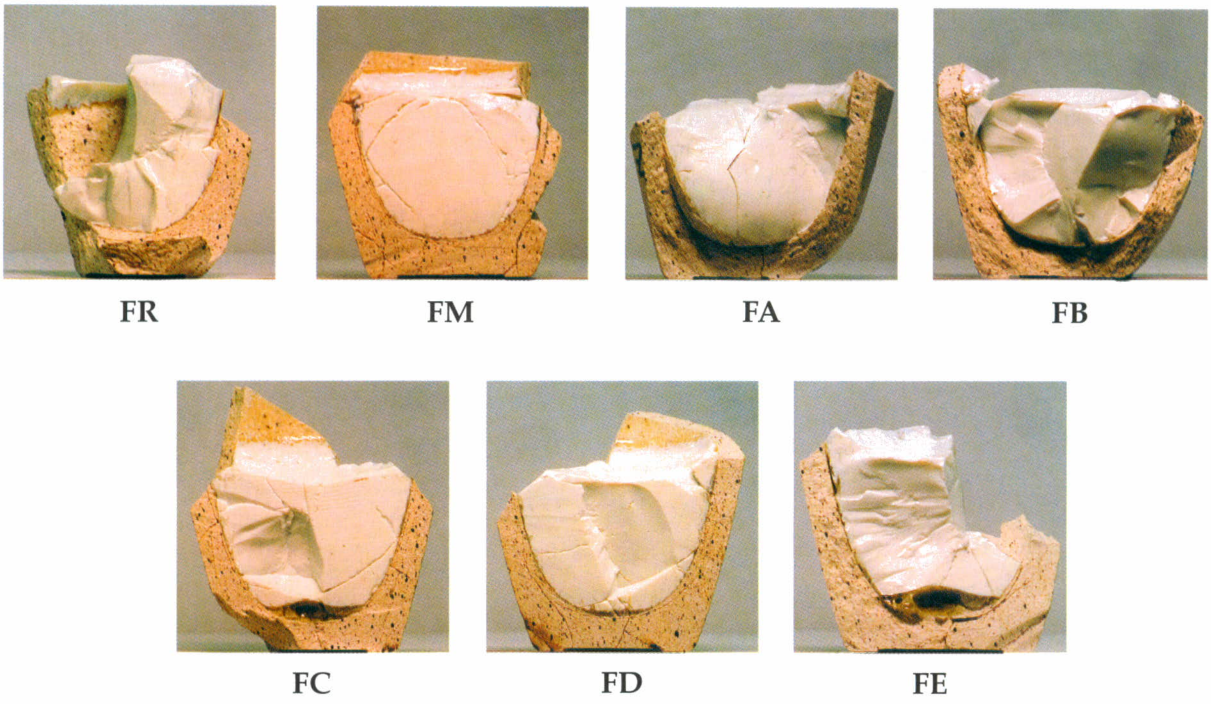
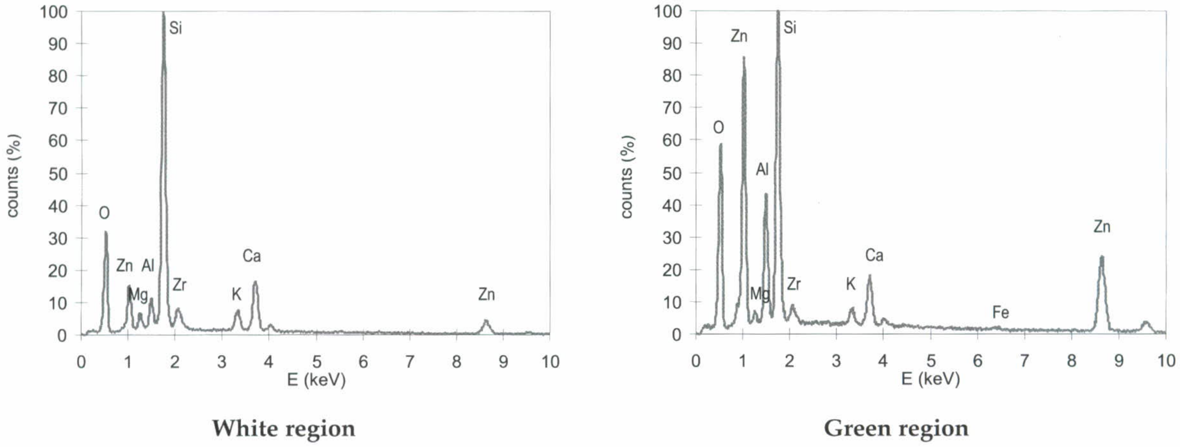
[6] Fernández, J.Mª. *El vidrio.* 2ª ed. Madrid: CSIC, 1991.



FR FM FA FB

FC FD FE

Figure 6. Cross section of the crucibles containing the diferent mixtures fused at 1600°C.



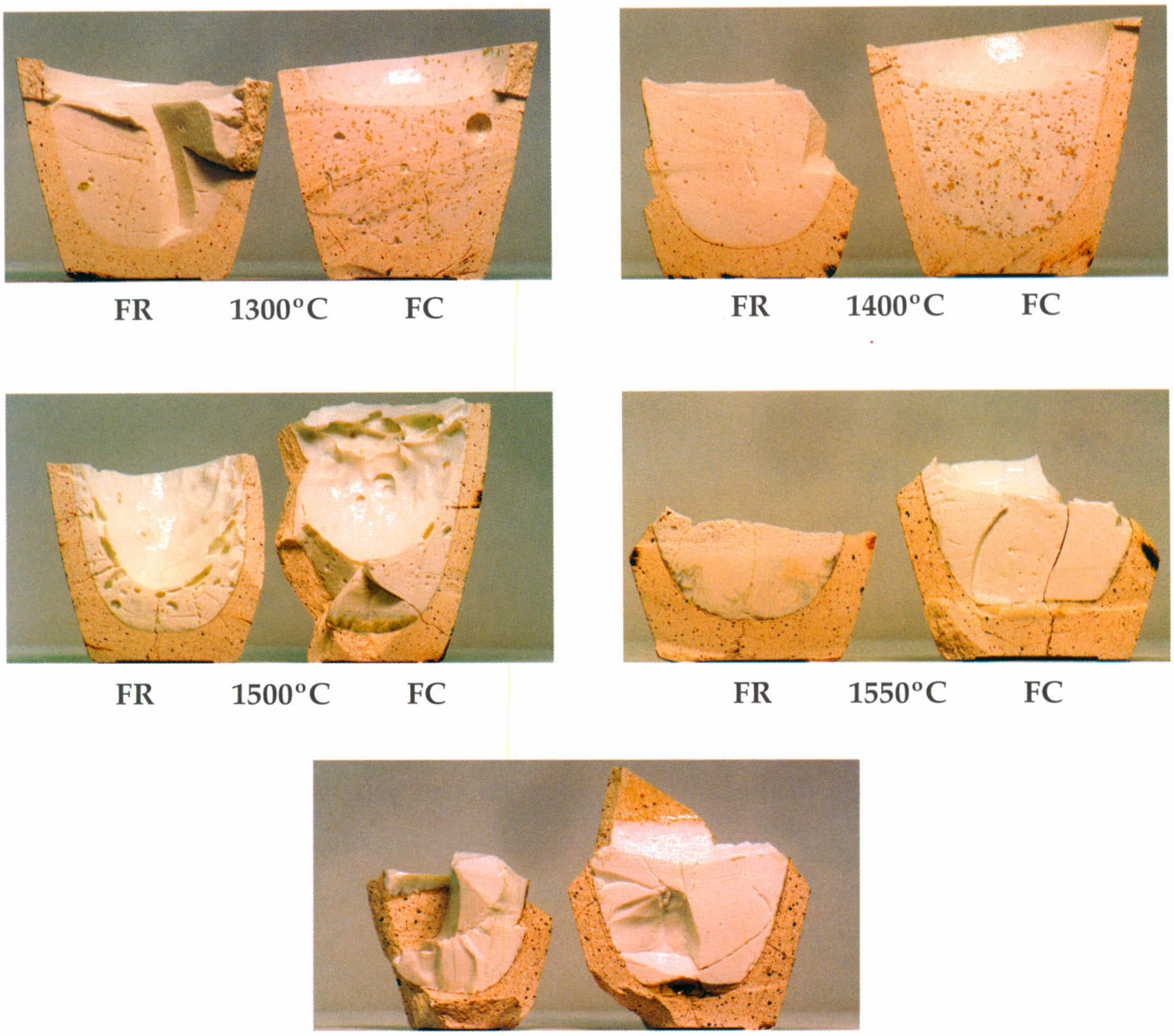
White region **Green region**

Figure 7. EDXA of the two regions of sample FC

3.2.2.3.- *Monitoring the fusion process*

In view of the foregoing findings, the fusion process of samples FR and FC was monitored to establish if there were any differences between using a non-granulated and a granulated zinc oxide.

The test used to determine the amount of foam was now performed again at the following different peak fusion temperatures: 1300, 1400, 1500, 1550 and 1600°C. The crucibles containing the mixtures fused at each temperature were cooled to room temperature and then cross-sectionally sliced. Figure 8 presents the photographs of the crucibles obtained at each test temperature.



FR 1300°C FC

FR 1400°C FC

FR 1500°C FC

FR 1550°C FC

FR 1600°C FC

Figure 8. *Cross section of the crucibles with samples FR and FC obtained at different fusion temperatures.*

The raw materials mixture underwent a sharp change between 1400 and 1500°C. The samples exhibited a much more fused appearance at 1500°C than at lower temperatures. In this temperature range, the mixtures rose in the crucible owing to the drop in viscosity of the glassy phase that formed, which favoured outgassing. The FR melt reached a greater height in the crucible than the FC melt, owing to its lower viscosity.

At 1550°C sample FR presented a line defining two clearly differentiated regions, a lower region without any bubbles and an upper region with a considerable quantity of bubbles. This did not occur in sample FC, which exhibited bubbles throughout the melt. Figure 9 shows photographs of a cross section of these test specimens taken with an optical microscope after embedding the specimens in resin and polishing them. The differences observed between the two samples also indicate that glassy-phase viscosity at 1550°C was lower in sample FR, as the gases it contained were more readily removed.

Figure 10 presents the photographs of the same two samples fused at 1600°C. The FR melt contains virtually no bubbles, as outgassing has been completed. However, sample FC still holds bubbles, especially in the upper area. As in the previous cases, this indicates that sample FC viscosity was higher, so that the bubbles were harder to clear.

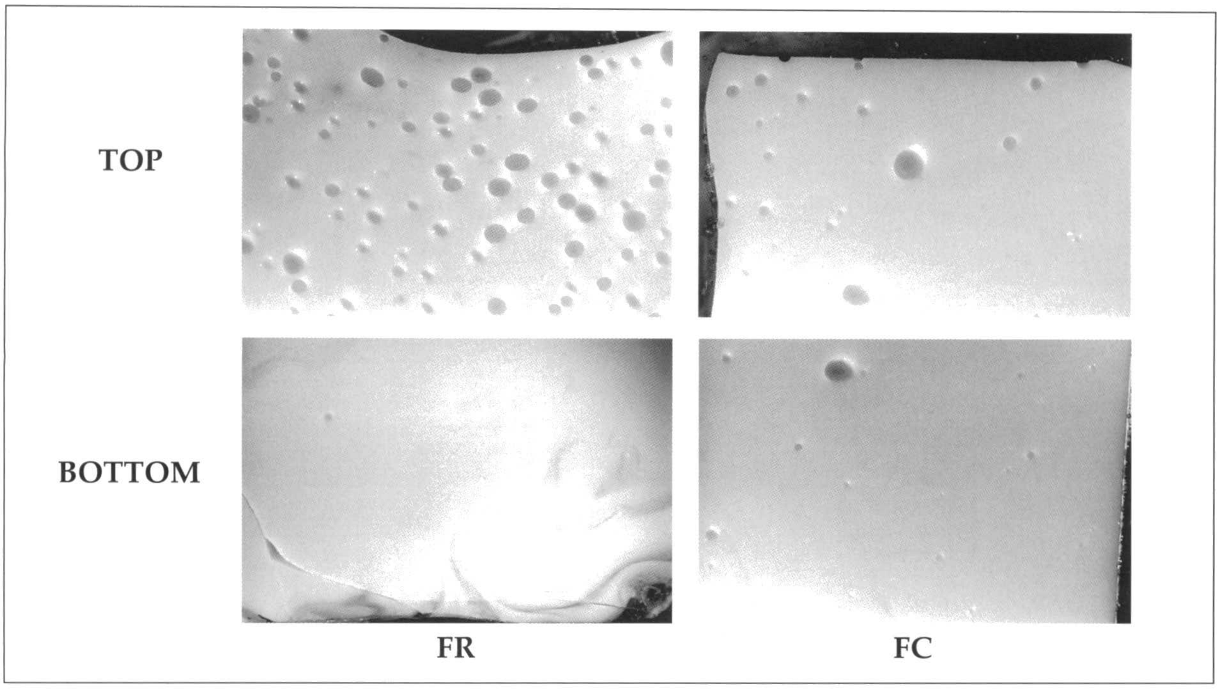


Figure 9. Cross section of the crucibles containing the samples fused at 1550°C

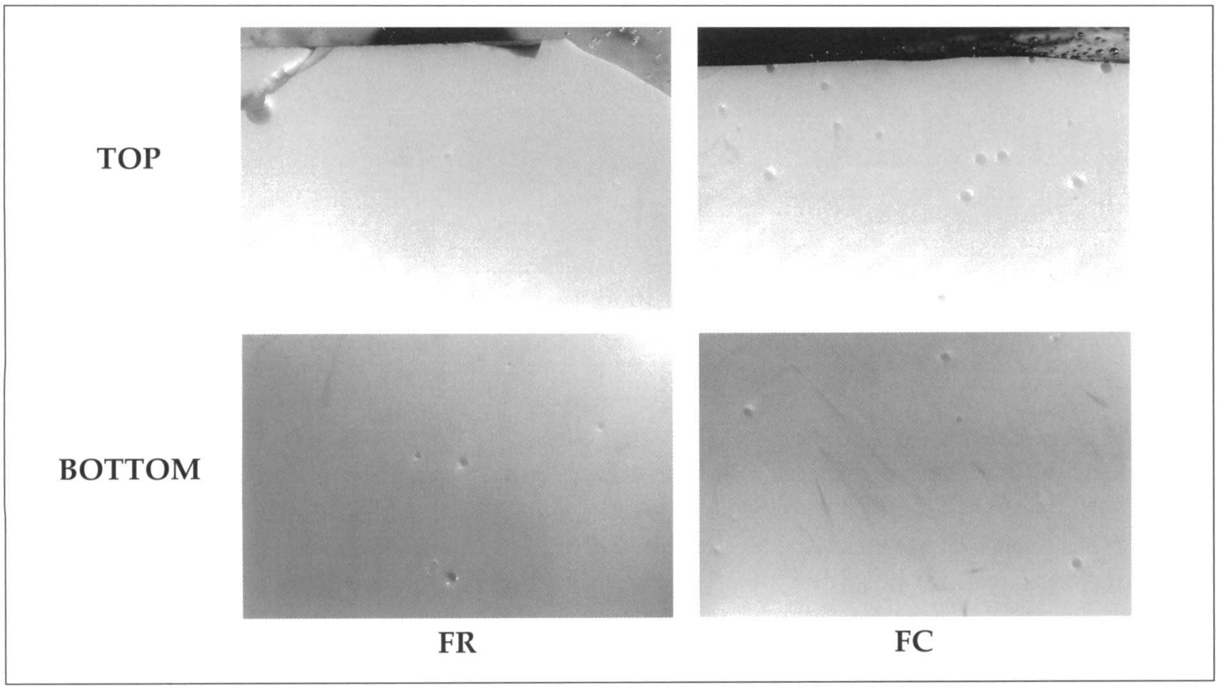
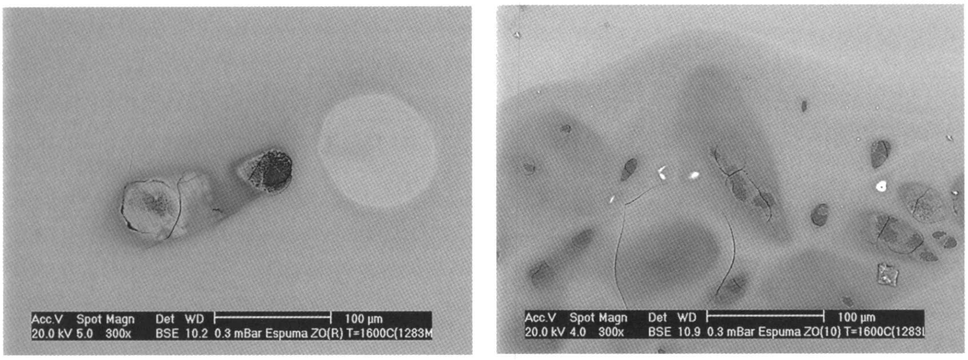


Figure 10. Cross section of the crucibles containing the samples fused at 1600°C.

The surface of the samples obtained at 1600°C was studied by electron microscopy (figure 11). Sample FC exhibited some unmelted zirconium silicate inclusions (white particles), which were not found in FR, as well as a larger quantity of unmelted quartz (dark-coloured particles). As already indicated, the presence of unmelted particles was encouraged by high glassy-phase viscosity, which impeded appropriate dissolution of the most refractory raw materials (quartz and zirconium silicate). This fact again appears to confirm what has already been remarked: glassy-phase viscosity was higher in the sample containing granulated zinc oxide as a raw material.



FR **FC**

Figure 11. *SEM images of the crucibles containing the samples obtained at 1600°C.*

As zinc oxide incorporation into the molten phase caused melt viscosity to drop, the greater viscosity of the melt containing granulated zinc oxide could stem from retarded zinc oxide incorporation into the glassy phase. With a view to confirming this fact, XRD scans were performed to determine the existing crystalline species in both samples (FR and FC) at a fusion temperature of 1300°C. The lowest test temperature was chosen, as the quantity of crystalline phases found is larger, making them easier to identify. The results are set out in table 4, which lists the intensity of the characteristic crystalline-phase peaks that were identified.

In sample FR the only detected crystalline phases were quartz (SiO_2) and zircon ($ZrSiO_4$), whereas in sample FC, besides these two phases, zincite (ZnO) and potassium feldspar were also detected, indicating retarded fusion on using zinc oxide agglomerates.

Crystalline species	Peak intensity	
	FR	FC
Zincite	0	511
Quartz	986	1475
Zircon	1246	1149
Potassium feldspar	0	114

Table 4. *Crystalline species present in samples FR and FC obtained at 1300°C.*

In sample FC furthermore, at temperatures of 1300 and 1400°C (figure 8), green spots were found throughout the melt. These appeared to correspond to undissolved zinc oxide agglomerates. With a view to determining the nature of these spots, a part of the crucibles with the FR and FC mixtures fused at 1400°C was studied by SEM (figure 12).

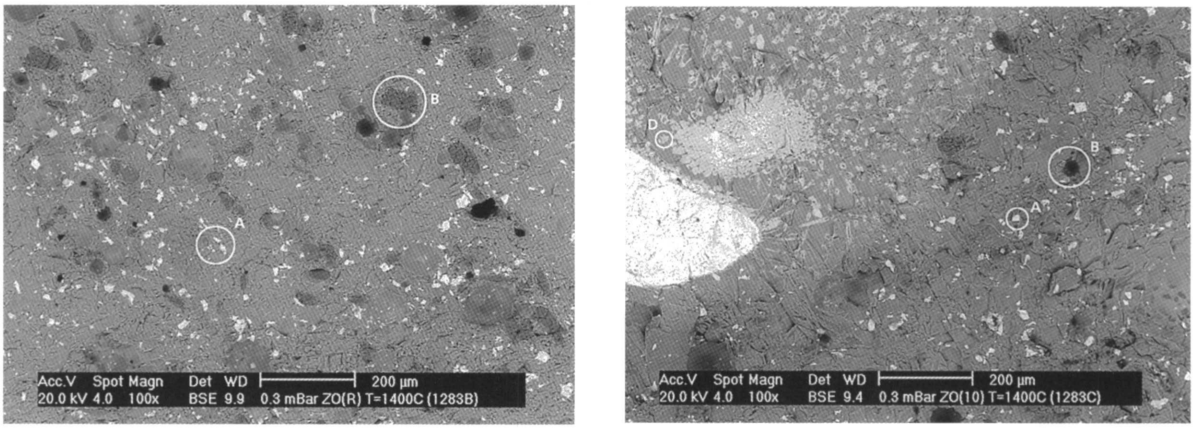


Figure 12. *SEM images of the samples obtained at 1400°C.*

Both melts exhibited small-sized light-coloured particles (15 to 30 μm), corresponding to unmelted zirconium silicate particles (A). Some dark particles sized around 40 μm (B) were also observed. Analysis revealed these to be undissolved quartz particles. Some white agglomerates (C) were only found in sample FC. Analysis showed these to be very porous zinc oxide agglomerates, which in certain cases attained a size of 1100 μm. Willemite crystals (Zn_2SiO_4) (D) appeared around these agglomerates, owing to the high zinc content of the glass in this area. These crystals were possibly produced by devitrification during cooling, as they were not likely to exist at fusion temperature.

These undissolved zinc oxide agglomerates exhibited a tendency to settle, as may be clearly observed in sample FC at 1500°C. Four domains can be distinguished at this temperature in the lower part of the crucible: a green region close to the crucible wall, a matt white region, a bluish region and finally a region corresponding to the material as a whole.

Each region was studied and analysed by SEM. The findings were as follows:

- *Green region close to the crucible wall:* Zinc oxide agglomerates surrounded by willemite particles ($Zn2SiO_4$).
- *Matt white region:* Willemite crystals with sizes ranging from 25 to 500 μm.
- *Bluish region:* Zinc-rich glassy phase.
- *Glossy white region:* This corresponded to the major glassy phase contained in the crucible, which exhibited numerous unmelted zirconium silicate inclusions and some unmelted quartz inclusions.

This suggests that zinc oxide settles during the fusion process, reaching the bottom of the crucible and enriching this area with zinc oxide, which favours subsequent willemite crystal formation. As mentioned above, these crystals could have formed by devitrification during cooling. They were unlikely to exist at fusion temperature.

At 1550°C sample FC exhibited a matt white region mainly consisting of willemite crystals close to the crucible wall, which resembled the matt white area found at 1500°C. At the highest test temperature (1600°C) the zinc oxide granules dissolved, yielding a zinc-rich transparent green glass. These inhomogeneities in the melt did not appear at any of the tested fusion temperatures in sample FR.

The conclusion may be drawn from all these tests that powdered zinc oxide is incorporated into the glassy phase at temperatures below 1300°C, whereas the incorporation of zinc oxide agglomerates larger than 700 μm occurs at temperatures exceeding 1500°C. Furthermore, large zinc oxide agglomerates settle during the fusion process, giving rise to inhomogeneities in the glassy-phase composition.

3.3 CONCLUSIONS

The following conclusions can be drawn from the study:

- The use of medium-size granulated zinc oxide, equal to or larger than 350 μm (samples B, C, D and E), as a raw material in the frit production process encouraged the formation of foam and the appearance of unmelted inclusions as a result of the retarded incorporation of zinc oxide into the glassy phase. This delay means that the removal of gases and the dissolution of unmelted materials occurs at a higher temperature, as the viscosity of the glassy phase is higher at a given temperature because it contains less zinc oxide.

- The use of medium-size granulated zinc oxide, equal to or smaller than 200 µm (samples A and M), did not give rise to any noticeable change in the frit production process or in the properties of the resulting glazes.
- The zinc oxide granules larger than 700 µm (samples C, D and E) settled during the fusion process, producing two clearly distinguishable glassy phases, one of which was considerably richer in zinc than the other.

4. INDUSTRIAL-SCALE TRIALS

As zinc oxide samples M and A did not give rise to any problems in the fusion process or changes in the resulting frit and glaze properties, it was decided to run a series of industrial trials to verify that no counter effects would arise in an industrial kiln and to ensure that the benefits found in handling, mixing and conveying would really provide a definitive advantage on using compacted zinc oxides instead of powder.

Industrial tests were performed in several frit-producing companies in Spain and Italy. The main conclusions were as follows:

1.- With the medium-size granulated zinc oxide (samples type A and M) no change was observed in the fusion process compared to powder; the quality of the resulting frits was fully comparable to that obtained with zinc oxide powder.

2.- Very significant improvements were found in handling and mixing:

  - In automatic installations, the medium-size granulated zinc oxide completely suppressed "waiting times" in weighing devices, yielding higher production rates. Order of magnitude: 20 waiting times per day with powder versus zero with sample M.
  - It was also found that the improved weighing accuracy could lead to savings in zinc oxide consumption of up to 5% by avoiding "over weighing" (commonly as high as 3%).
  - Improvement in operator working conditions (fewer manual interventions, less maintenance). In manual installations these advantages were heightened due to the complementary benefits stemming from manipulating a dust-free product causing no more inhalation or skin exposure.

3.- Tests on stack emissions were less clear, possibly due to measuring difficulties and lack of precise instrumentation.

Nevertheless, one company reported having been obliged to modify the composition of the mix (lowering zinc oxide amount in granules) to obtain the same zinc content in the frits, which is probably linked to the kind of facility used in frit production.

5. OVERALL CONCLUSIONS

The use of medium-size granulated zinc oxide did not give rise to any disadvantages or noticeable changes in the frit melting process or in the properties of the resulting glazes in the industrial installations. On the contrary, advantages qualified as very significant by several frit producers were found on using sample M:

- savings in weighing devices
- savings in handling devices
- savings in zinc oxide consumption
- improved operator working conditions
- in the case of manual handling: healthier working conditions through less inhalation and skin exposure.