STUDY OF POROSITY IN SINGLE FIRING GLAZES FOR FLOOR TILING

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1. INTRODUCTION

The characteristics of the glazed surface, both technical and aesthetic, are determined by various factors, amongst which is the existence of pores inside the layer of glaze.

The porosity of ceramic glazes is of decisive importance for the end quality of glazed floor tiling products. For over time the glaze undergoes surface wear due to the continuous abrasion produced by contact with materials of a hardness equal to or greater than its own. This surface wear leads to its interior pores being left in contact with the exterior environment, thus facilitating the penetration of foreign matter (dirtiness, organic liquids, etc.) into these pores, with the consequent loss of aesthetic characteristics in the finished product.

Similarly, some surface defects (puncturing, pockets, etc.) are caused by bubbles in the glaze which rise to the surface during the firing process, remaining there subsequently following the product cooling phase (1) (2) (3) (4) (5) (6) (7) (8) (9) (10).

2. OBJECTIVE AND SCOPE OF THIS RESEARCH

From the above outline the need emerges to be aware of the development of porosity in a ceramic glaze and for determination of the variables upon which it depends, all this with a view to reducing as far as possible porosity in the ceramic glaze.

In order to achieve these objectives an experimental work plan was drawn up in order to determine the influence on porosity of the ceramic glazes used for flooring of glaze composition, firing temperature and thickness of the glaze layer.

3. MATERIALS AND PROCEDURE

3.1. CHARACTERIZATION OF MATERIALS

3.1.1. Fritted material

In order to determine the influence of the nature and content of the fritted material on the development of porosity recourse was had, suitably combining various industrial frits, of the glass phases whose chemical composition, expressed in moles, is detailed in Table I.

Figures 1, 2, 3 and 4 give details of the wetting angle and the length of the fall globule for each of the compositions described above. Surface tension was determined theoretically on the basis of the Dietzel expression, obtaining the values shown in Figures 5 and 6. (11)

3.1.2. Glazes

In order to determine the influence exercised by the thickness of the glaze layer and the firing temperature on resulting porosity, a glaze widely used in the manufacture of single firing ceramic flooring was employed. Its batch formula is detailed in Table II, as composition 1.

For the experiments designed to study the influence of the various components (frits and additives) on resulting glaze porosity, this industrial glaze was modified to produce a series of glazes whose batch formulae are shown in Table II.

3.1.3. Additives

The nature and characteristics of the additives used in the formulation of the glaze additives is shown in Table III.

3.1.4. Dressing

Recourse was had to a dressing of fritted material and additives widely used in single firing flooring manufacture.

3.1.5. Base

The experiments were carried out using a base of single firing stoneware pressed industrially at 220 kg/cm2 and 5% humidity from atomization. The apparent density of the resulting piece is 2.05 g/cm3. The industrial pieces of 20 x 30 cm2 were cut to obtain test specimens of 10 x 10 cm2.

The atomization comprised red clays, basically illitic- kaolin (with predominance of the illitic structure), with abundant quartz and iron oxide.

3.2. EXPERIMENTAL PROCEDURE

3.2.1. Preparation and application of glazes

The compositions of the glazes were prepared by milling the materials by humid process with alumina-ball mills of 500 cm3 capacity, up to 4% rejection in weight on screen of 45 micra. The prepared slips, at a density of 1.65 g/cm3, were applied on pieces of 30 x 30 cm2 single firing stoneware base, using spray gun with air pressure of 5 kg/cm2. 70 g of glaze was deposited on each piece.

For those experiments designed to determine the influence of the glaze layer on porosity, the quantities of glazes applied were 40, 100 and 140 g per piece. The dressing preparation conditions were: 1.55 g/cm3 density and 0.5% rejection of milling at 45 micra. The quantity of dressing used was kept constant at 25 g per piece.

3.2.2. Firing of the glazes

All firings were carried out in rapid-cycle electric laboratory kiln with controlled temperature and low thermal inertia, with good temperature uniformity throughout the chamber. Trials were made using similar firing cycles, differing from each other only in the maximum firing temperature. Pieces were held at that temperature for six minutes. The heating and cooling slopes used in all laboratory firings is shown in Figure 7, together with the slope corresponding to industrial firing.

3.2.3. Determination of pore size and distribution in the fired glaze

Determination of the number and size of the pores was carried out on the basis of observation of the fired pieces (at different temperatures) under an optical microscope. Preparation of the test specimens was carried out by embedding with a resin and polishing the transversally- cut samples from each of the pieces. Subsequently, in order to observe and determine the percentage and sizes of the pores, the test specimen was covered with a layer of graphite powder, so that it could penetrate inside the pores of the glaze. Excess graphite (which had not penetrated the pores) was then removed by rubbing the cutting surface lightly with sandpaper.

The occupied surface area ratio of pores/total surface area (Sp/St) and the size of the pores was determined by image analysis in a piece of equipment (Optomox V) especially designed for the purpose. All test specimens were 60 mm in length.

For each test specimen the image analyser supplies the pore surface/total surface area (Sp/St) ratio in the form of a bar diagram, thus allowing deduction of the average value for the test specimen as a whole and spot values for each of the zones where the determination was carried out (30-40). For the sake of simplification, only the average porosity values are expressed in the results (Figure 8).

The results corresponding to pore size distribution for each test specimen can likewise be expressed in the form of frequency histograms based either on the number of pores (Figure 9) or on the volume which they occupy (Figure 10). As can be seen from these figures, the average diameter based on the number of pores takes excessive account of pores of small size. The average volumetric diameter, on the other hand, is much more sensitive than the first method to the presence of pores of large size. The latter method therefore appears to be more suitable for characterization of average pore size by means of a simple parameter. For some special cases, however, the complete distribution of pore size will be included.

3.2.4. Determination of the nature and size of phases present in the fired glaze

This determination was made by observation of the fired and polished test specimens under a sweep microscope. The chemical composition of the phases present in the glaze was determined using dispersive energy microanalysis equipment.

4.RESULTS AND DISCUSSION

4.1. INFLUENCE OF FIRING TEMPERATURE ON THE MICROSTRUCTURE OF THE GLAZE

4.1.1. Nature and size of the phases present

As firing temperature increases, the viscosity of the glass phase diminishes, revealing itself in increased partial dissolution of the glaze additives. The proportion in which each of them dissolves, however, is quite different. Thus, for example, at low firing temperatures (Figure 11) and using a sweep microscope, the following is observed:

- Nuclei of nepheline surrounded by a extensive layer of glaze with high content of Al, Si and Ca, which reveals that this phase has dissolved to a considerable extent.

- Particles of quartz surrounded by a layer of glaze with very high silicon content owing to the partial dissolution of the quartz. Unlike the nepheline, this layer of glaze is much narrower, which indicates that quartz dissolution is lower than in the previous phase.

- Particles of alumina presenting diffuse grain limits due to incipient dissolution of that phase.

- Particles of $ZrSiO_4$ of two different sizes. The smaller ones, concentrated in more or less

extensive areas, proceed from crystallization on the basis of glaze with high zirconium content. The larger particles are those added to the glaze mix, which do not present the characteristic aureola indicating partial dissolution of the phase.

At higher temperatures (Figures 12 and 13) dissolution of the nepheline, alumina and quartz was more extensive, while the added particles of ZrSiO4 did not present any appreciable change. As occurred at lower temperatures, the nepheline dissolves more than the quartz, and the quartz in its turn more than the alumina. Thus, at 1150°C the only quartz particles observed are those of large size, while alumina particles of smaller size can still be identified.

A slight increase can also be observed in the particle size of the ZrSiO4 which crystallizes from the glass phase with the increase of temperature.

It emerges from the above that this progressive dissolution of some of the additives used will considerably affect the viscosity of the glaze mixture. The reduction in viscosity of the glaze with increase in firing temperature will in fact be much less than that which would arise in the absence of quartz or corundum, for when these dissolve they enrich the glass phase with silicon, which tends to increase the viscosity of the phase.

4.1.2. Porosity and distribution of pore size

As the firing temperature increases there is a considerable reduction of glaze viscosity and, to a lesser extent, of surface tension; both factors favour increased size of the fused bubbles, as can be seen in Figure 14 for glaze 1. The mechanisms causing this increase of average particle size are as follows:

i) Coalescence of pores. As can be observed in Figure 14, increased firing temperature leads to a reduction in the number of pores/mm of the glaze. Nevertheless, on comparing distributions of pore size (Figure 15) it is found that the pores of small diameter fall (in number and volume) considerably as temperature increases, while the larger ones increase (in number and size).

ii) Increased volume of occluded gas. At normal glaze maturation temperatures the viscosity and surface tension of the glaze are sufficiently viscous to permit an increase in pore volume owing to thermal expansion of the occluded gas and/or to generation of gases by reaction between the components of the glaze.

For this glaze, the increase in pore size with temperature leads to a progressive increase in its porosity. These results are consistent with those obtained for other glazes, which in melted form also do not present sufficiently low viscosity to allow the pores to reach the size of the thickness of the glaze layer, subsequently escaping from that layer. As indicated in the bibliography, fining of the glaze can only be carried out with very low viscosity glazes. With viscous glazes such as the one under study, increased temperature increases the volume and size of the pores.

4.2. INFLUENCE OF THICKNESS OF GLAZE LAYER ON RESULTING POROSITY

Figures 16 and 17 show the variation of surface area quotient occupied by pores/total surface area (Sp/St), expressed as a percentage, and that of equivalent pore diameter (Dv) compared to thickness of the glaze layer for the three maximum firing temperatures used.

Examination thereof reveals that both the porosity (Sp/St) and pore size increase lineally as thickness of the glaze layer increases. It can likewise be observed that the effect of temperature on porosity and average pore size is that they increase the greater the thickness of the glaze layer. In fact, for small thicknesses of glaze, increasing firing temperature from 1110°C to 1150°C produces a slight increase in porosity and pore size; on the other hand, for a glaze layer thickness of 250 μm, the same temperature increase leads to a considerable increase in the volume and size of the pores.

These results are consistent with those obtained by other researchers studying the effect of the

glaze layer on the size and number of bubbles in pieces of porcelain fired in traditional firing cycles (13/14). The increase of pore size with increased glaze thickness is probably due the fact that as the glaze layer increases the bubble can reach a greater size before it bursts and disappears. Similarly, as the thickness of the glaze layer increases so too does the time necessary for the bubbles to move from the glaze and/or from the glaze/base interface to the surface, so that a greater number of bubbles will be retained and the total porosity of the glaze will thus increase.

The marked influence of thickness of the glaze layer on the volume and size of the glaze pores makes it essential to carry out exhaustive control of that parameter during preparation in order to avoid the defects associated with the presence of pores in the glaze.

4.3. INFLUENCE OF COMPOSITION OF THE GLAZE ON ITS RESULTING POROSITY

4.3.1. Influence of the nature of the fritted material

In order to determine the influence of the nature of the fritted material, a series of compositions were formulated in which the proportion of additives was kept constant, with only the composition of the initial fritted material varying (compositions 1, 2, 3, 4, 5 and 6 of Table II).

Figure 18 shows the results for compositions 2, 3 and 4. It can be observed that as the melted viscosity (Figure 3) and surface tension (Figure 5) of the fritted material increase, so too does the average size of the pores and the porosity of the resulting glaze.

It can likewise be observed that the increase in pore size and of general porosity of the three glazes with temperature is greater the lower the melted viscosity of the fritted material. Composition 4 in fact presents increased average pore size with temperature which is greater than composition 3, while the latter is in turn greater than composition 2. Porosity follows a parallel evolution, with the exception of composition 4, which at 1150°C presents lower porosity than at 1100°C. This apparent anomaly is due to the fact that at 1150°C the average diameter of the pores is similar to the thickness of the glaze layer, so that many of them escape and the piece is noticeably punctured.

Figure 19 shows the results corresponding to compositions 1, 5 and 6 (Table II). These compositions differ from each other basically in the PbO content of the fritted material. As happened with the above compositions, it was found that a decrease in the viscosity and surface tension of the fritted material (Figures 4 and 6) increased porosity and average pore size, both rising with temperature.

4.3.2. Influence of the fritted material content

Figure 20 shows the results corresponding to compositions 1, 7 and 8 (Table II). These differ from each other in their fritted material content. It can be observed that as the fritted material content rises the porosity and average pore size of the glaze composition and the resulting glaze also increases. This is due to the viscosity of the glaze - which is in the last analysis the property which governs the size and volume of the pores - increasing as the frit content rises.

4.3.3. Influence of the nature and content of the additives

Figure 21 shows the results of compositions which differ from each other in their content of zirconium silicate (compositions 1, 9 and 10, Table II).

With the exception of the 1150°C firing temperature, it can be observed that the porosity and average pore size of the glaze increase with zirconium silicate content.

The most probable explanation for this is that as the number of zirconium silicate particles in the glaze increases there are a greater number of bubbles in the melt which may anchor themselves to the particles, thus encouraging coalescence of the pores and increasing the resulting porosity. The

fact that at 1150°C, composition 10, with lower zirconium silicate content (and therefore a larger proportion of fritted material), presents exceptionally high porosity and average pore size when compared to lower temperatures is due to excessive lowering of the glaze viscosity through excessive glass phase.

The influence of nepheline content on porosity and average pore size is shown in Figure 22. In interpreting these results it should be borne in mind that with any change in the proportion of nepheline in the glaze there is a perceptible change in the quantity of liquid phase and its viscosity in the melt, for as was seen above (section 4.1.1.) that phase dissolves easily in the liquid phase of the glaze. Thus, by considerably increasing the proportion of this phase in the glaze the proportion of liquid phase in the melt is increased, which tends to increase pore size and porosity. On the contrary, increasing the proportion of nepheline increases the viscosity of the glass phase, for it becomes enriched in SiO2 and Al2O3, which tends to reduce porosity and pore size. The combination of both opposing effects means that for this type of glaze the most suitable porosity and pore size present themselves for the nepheline content of composition 1.

Figure 23 shows the porosity and average pore size values obtained by eliminating from composition 1 corundum (composition 13), quartz (composition 14) and calcium carbonate (composition 15). Examination of this reveals that eliminating quartz and corundum from the batch composition increases porosity and average grain size of the resulting glaze at the three temperatures tested. The probable explanation for this is that elimination of these additives from the glaze means, as we saw above, that they are considerably dissolved in the liquid phase and that the latter's viscosity is perceptibly reduced, which encourages growth of pore size and increased porosity of the resulting glaze.

On the contrary, eliminating calcium carbonate from the glaze composition leads to considerably reduced porosity and average pore size. This is due on the one hand to the viscosity of the carbonate-free glaze being much higher than that of composition 1 and, on the other hand, to the fact that the calcium carbonate, as it decomposes at relatively high temperatures, is a probable source of bubbles in the glaze, due to the generation of gases.

4.4. INFLUENCE OF THE GRANULOMETRIC DISTRIBUTION OF THE GLAZE ADDITIVES ON ITS RESULTING POROSITY

Figure 24 shows the results obtained for compositions 16, 17 and 18 (Table II). These differ from each other in distribution of the particle size of the quartz which is added to the glaze (Table II). Figures 25 and 26 compare the results obtained on modification of distribution of particle sizes of the corundum and calcium carbonate respectively. It is found in the three cases that, in general, porosity and average pore size of the resulting glaze decrease slightly with the average particle size of the additive. This is probably explained by the average pore size in the raw glaze decreasing with the particle size. The fact that the increase in porosity and average pore size with the particle size of the additive is greater for quartz and alumina than for the carbonate is due to the former not dissolving completely in the glaze, so that as their size increases so too does the size and number of crystalline particles which can hold bubbles in the glaze.

Figure 27 shows the results corresponding to compositions 25 and 26, in which the average particle size of the zirconium silicate has been modified considerably. It is found that the porosity and pore size of the two glazes is very different. This is probably due to the great difference of granulometic distribution used.

5. CONCLUSIONS

The following conclusions may be drawn from the study carried out:

- It was found that in order to reduce to a minimum the porosity of a glaze it is essential that the glaze present a maturation interval which coincides with that of product firing.

- It was found that evolution of viscosity with temperature in the glass phases has a considerable influence on porosity and average pore size in the end product.

- The addition during firing of components which do not dissolve, or do so only to a limited extent, considerably increases pore size and volume in the glaze.

- Increasing the size of the additives which dissolve little during firing of the glaze leads to an increase in pore size and volume in the end product.

- It was found that porosity and average pore size increase lineally with the thickness of the glaze layer.

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	1	2	3	4	5	6
SiO_2	61.73	61.12	62.12	62.83	61.71	62.83
Al_2O_3	5.98	6.44	5.97	3.25	6.10	5.94
B_2O_3	3.62	—	7.81	—	3.74	3.53
Na_2O	2.27	2.77	2.08	0.30	2.33	2.22
K_2O	2.97	2.43	3.94	0.42	3.08	2.93
CaO	8.69	8.04	10.86	0.23	9.11	8.49
MgO	1.59	1.73	1.70	0.29	1.62	0.16
BaO	1.62	3.60	—	—	1.69	1.58
ZnO	6.30	13.86	—	—	6.57	6.16
PbO	2.66	—	—	32.69	1.39	3.89
ZrO_2	2.56	—	5.5	—	2.66	2.48

Table I. Chemical composition of the fritted material (% moles)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
GLASS PHASE 1	46	–	–	–	–	–	69	23	46	46	46	46	46	46	46
GLASS PHASE 2	–	46	–	–	–	–	–	–	–	–	–	–	–	–	–
GLASS PHASE 3	–	–	46	–	–	–	–	–	–	–	–	–	–	–	–
GLASS PHASE 4	–	–	–	46	–	–	–	–	–	–	–	–	–	–	–
GLASS PHASE 5	–	–	–	–	46	–	–	–	–	–	–	–	–	–	–
GLASS PHASE 6	–	–	–	–	–	46	–	–	–	–	–	–	–	–	–
ZIRCONIUM SILICATE 1	13	13	13	13	13	13	13	13	19.5	6.5	13	13	13	13	13
ALUMINA 1	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	–	7.5	7.5
NEPHELINE	23	23	23	23	23	23	23	23	23	23	39.5	11.5	23	23	23
QUARTZ 1	6	6	6	6	6	6	6	6	6	6	6	6	6	–	6
CALCIUM CARBONAE 1	5	5	5	5	5	5	5	5	5	5	5	5	5	5	–
KAOLIIN	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4

	16	17	18	19	20	21	22	23	24	25	26
GLASS PHASE 1	46	46	46	46	46	46	46	46	46	46	46
Zr SILICATE 1	13	13	13	13	13	13	13	13	13	13*	–
Zr SILICATE 2	–	–	–	–	–	–	–	–	–	–	13*
ALUMINA 1	7.5	7.5	7.5	–	–	–	7.5	7.5	7.5	7.5	7.5
ALUMINA 2	–	–	–	–	–	7.5*	–	–	–	–	–
ALUMINA 3	–	–	–	–	7.5*	–	–	–	–	–	–
ALUMINA 4	–	–	–	7.5*	–	–	–	–	–	–	–
NEPHELINA	23	23	23	23	23	23	23	23	23	23	23
QUARTZ 1	–	–	–	6	6	6	6	6	6	6	6
QUARTZ 2	–	–	6*	–	–	–	–	–	–	–	–
QUARTZ 3	–	6*	–	–	–	–	–	–	–	–	–
QUARZ 4	6*	–	–	–	–	–	–	–	–	–	–
CALCIUM CARB. 1	5	5	5	5	5	5	–	–	–	5	5
CALCIUM CARB. 2	–	–	–	–	–	–	–	–	5*	–	–
CALCIUM CARB. 3	–	–	–	–	–	–	–	5*	–	–	–
CALCIUM CARB. 4	–	–	–	–	–	–	5*	–	–	–	–
KAOLIN	4	4	4	4	4	4	4	4	4	4	4

Table II (cont'd) Batch formulae by weight.

(*) Addition carried out after milling.

EQUIVALENT DIAMETER (μm)	PERCENTAGE BY WEIGHT OF PARTICLES LOWER THAN D			
	ALUMINA 1	ALUMINA 2	ALUMINA 3	ALUMINA 4
40	36.4	100.0	97.4	90.7
20	27.3	98.0	91.0	85.2
10	13.8	85.5	73.0	68.9
4	2.4	25.5	23.4	11.8
2	1.8	8.0	8.8	4.5

Table III Granulometric distribution of additives.

EQUIVALENT DIAMETER (μm)	PERCENTAGE BY WEIGHT OF PARTICLES LOWER THAN D			
	QUARTZ 1	QUARTZ 2	QUARTZ 3	QUARTZ 4
40	71.9	100.0	91.9	80.7
20	54.6	88.0	55.1	62.1
10	33.1	65.0	46.9	39.5
4	18.0	37.5	25.7	20.2
2	12.2	23.5	16.5	14.1

Table III (Cont'd) Granulometric distribution of additives.

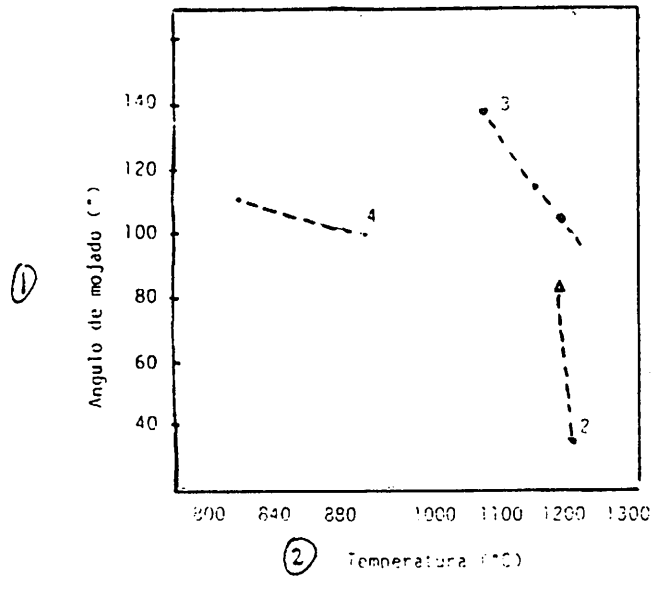
EQUIVALENT DIAMETER (μm)	PERCENTAGE BY WEIGHT OF PARTICLES LOWER THAN D			
	CALCIUM CARBOBATE 1	CALCIUM CARBOBATE 2	CALCIUM CARBOBATE 3	CALCIUM CARBOBATE 4
40	59.9	100.0	94.8	91.4
20	71.0	87.0	74.0	74.0
10	45.0	60.0	48.8	47.5
4	22.9	33.0	24.7	22.9
2	9.9	21.0	14.7	13.7

Table III (Cont'd) Granulometric distribution of additives.

EQUIVALENT DIAMETER (μm)	PERCENTAGE BY WEIGHT OF PARTICLES LOWER THAN D			
	NEPHELINE	KAOLIN	ZIRCONIUM SILICATE 1	ZIRCONIUM SILICATE 2
40	97.6	100.0	100.0	88.2
20	80.1	100.0	100.0	57.8
10	51.3	91.0	99.0	36.0
4	30.3	74.0	97.0	19.0
2	19.5	59.0	85.0	10.9

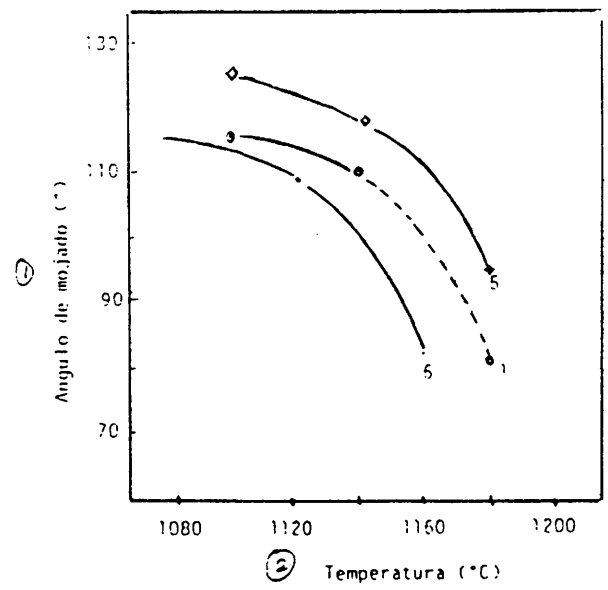
Table III (Cont'd) Granulometric distribution of additives.

FIGURAS



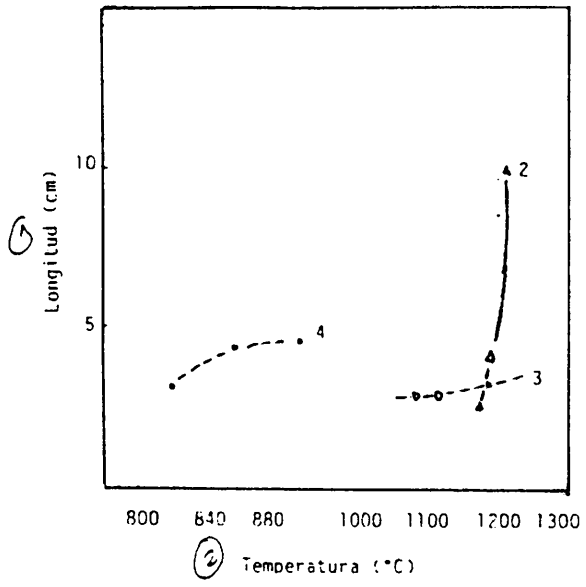
1) Angle of wetting (°)
2) Temperature (°C)

Figure 1.- Variation of angle of wetting with temperature of fritted material 2, 3 and 4.



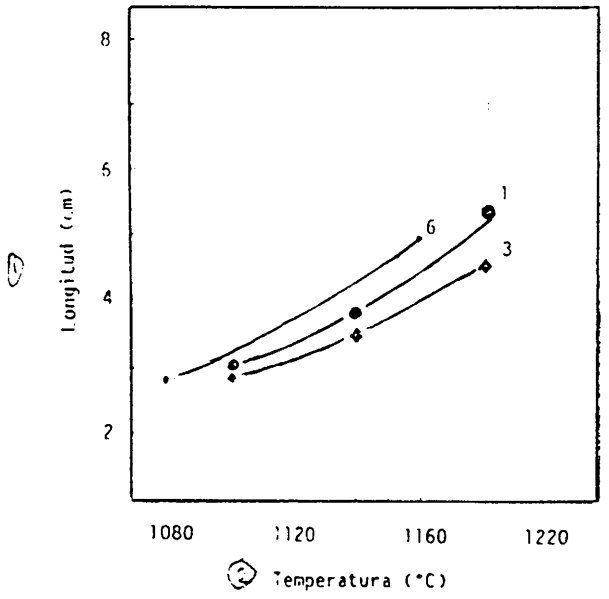
1) Angle of wetting (°)
2) Temperature (°C)

Figure 2.- Variation of angle of wetting with temperature of fritted material 1, 5 and 6.



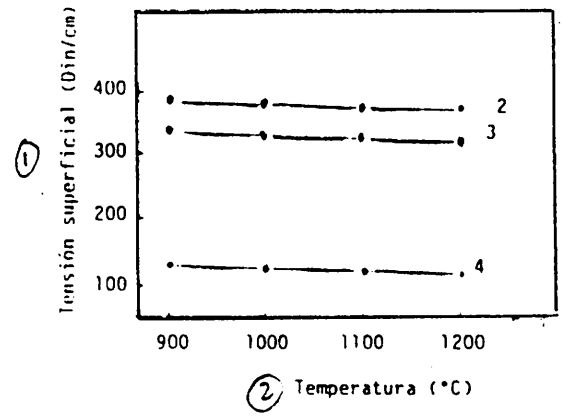
1) Length (cm)
2) Temperature (°C)

Figure 3.- Variation of length of fall globule with temperature of fritted material 2, 3 and 4.

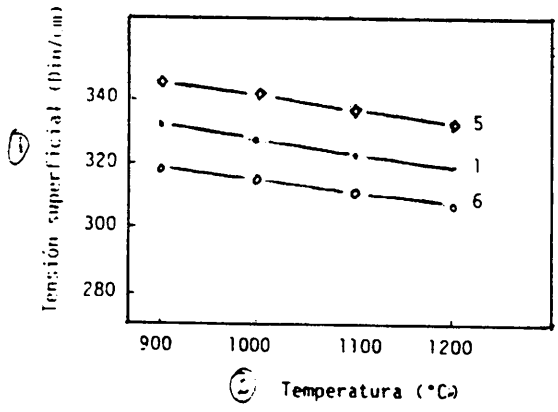


1) Length (cm)
2) Temperature (°C)

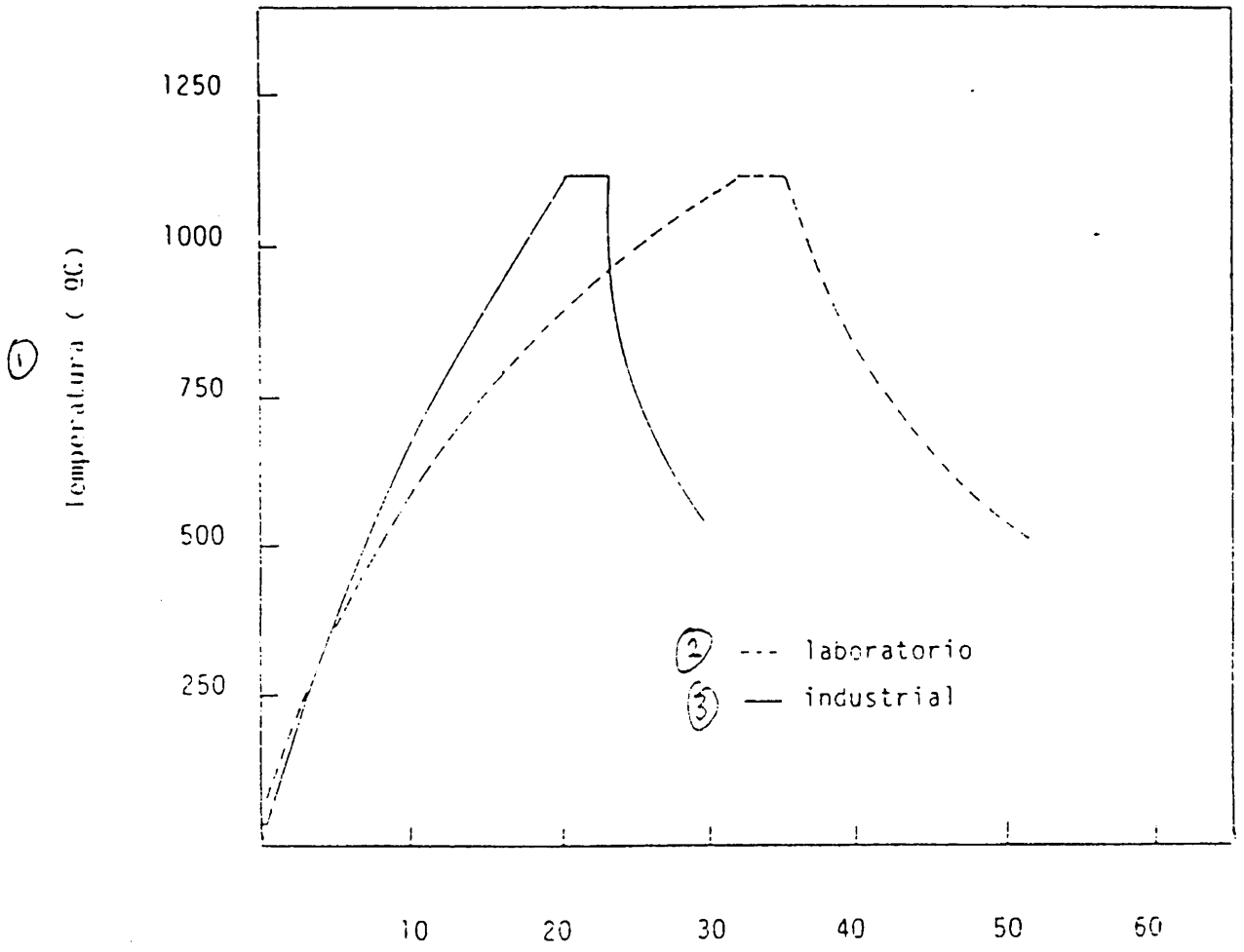
Figure 4.- Variation of length of fall globule with temperature of fritted material 1, 5 and 6.



1) Surface tension (Din/cm)
2) Temperature (°C)
3) Figure 5.- Variation of surface tension with temperature of glass phases 2, 3 and 4.

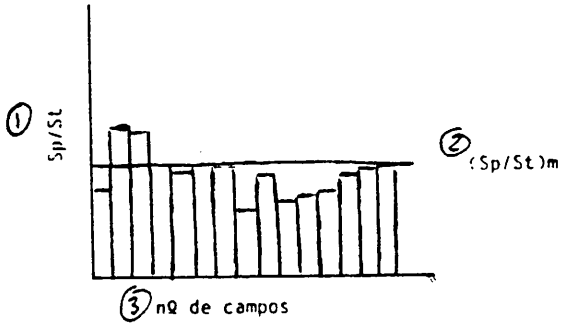


1) Surface tension (Din/cm)
2) Temperature (°C)
3) Figure 6.- Variation of surface tension with temperature of glass phases 1, 5 and 6.

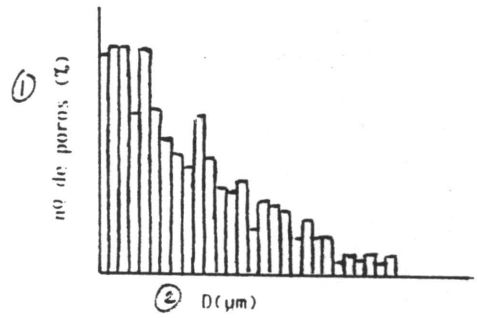


1) Temperature (°C)
2) laboratory
3) industrial
4) time (min.)

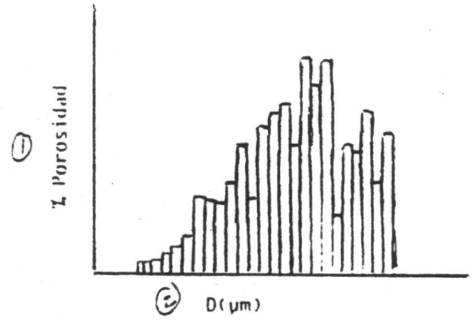
Figure 7. Laboratory and industrial firing cycles.



1) Sp/St 2) (Sp/St)m 3) No. of fields Figure 8.



1) No. of pores (%) 2) D(μm) 3) Figure 9.



1) % porosity 2)D(μm) 3) Figure 10

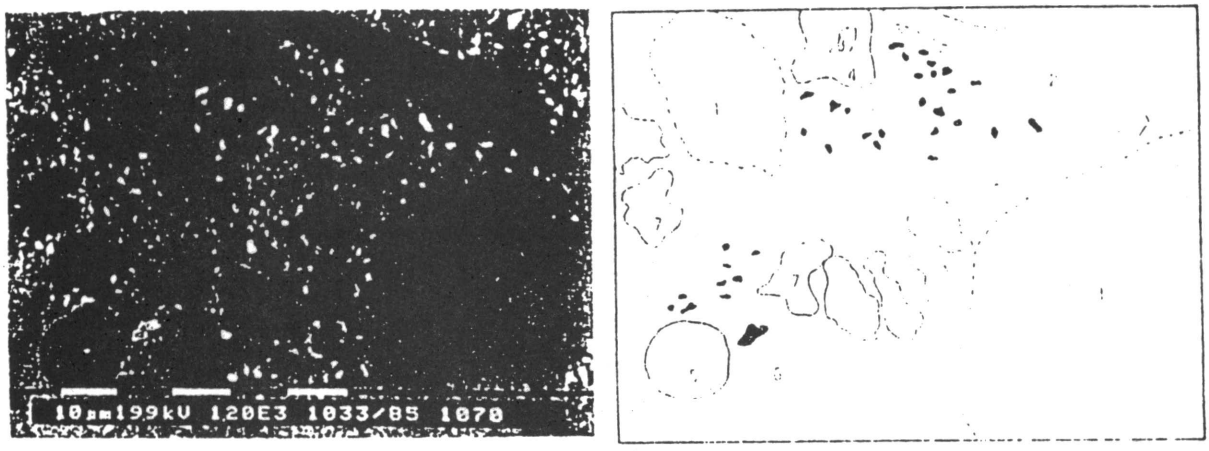


Figure 11.- Microphotography of glaze 1 fired at 1070°C. 1. Glaze without $ZrSiO_4$. 2. Quartz 3. Nepheline 4. Phase rich in Al Si Ca. 5. Pore 6. $ArSiO_4$ 7. Alumina.

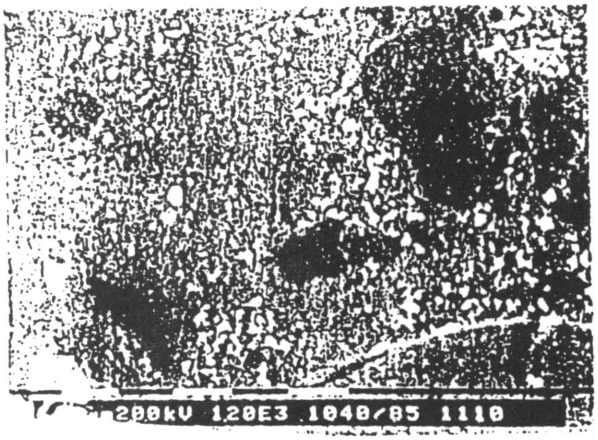


Figure 12.- Microphotography of glaze 1 fired at 1110°C.

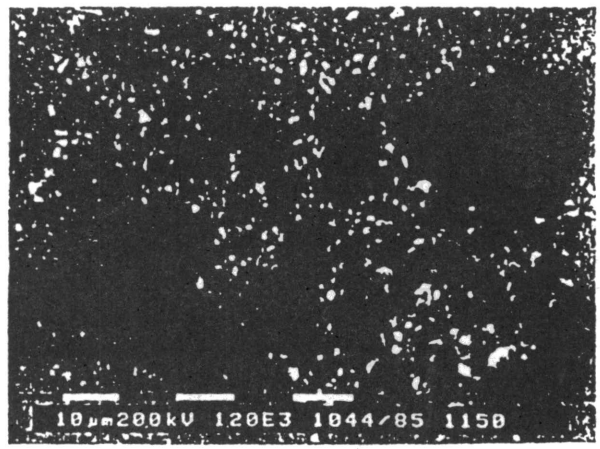
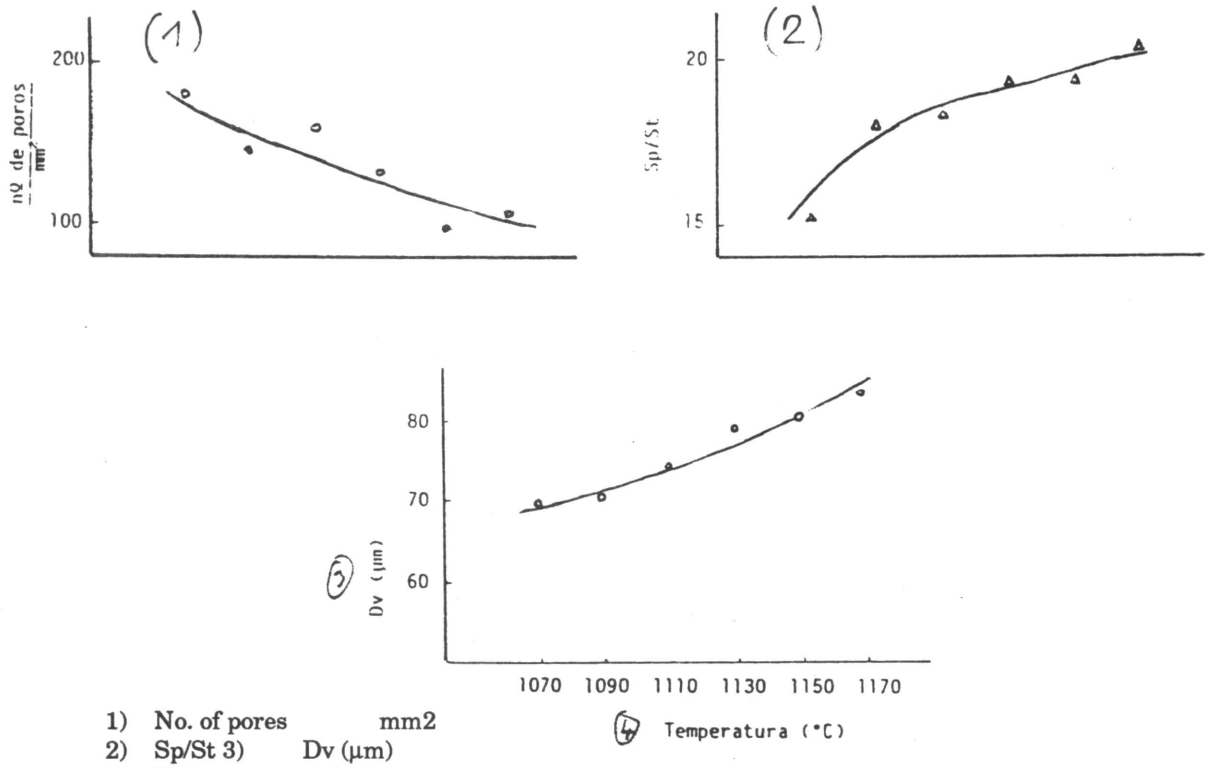
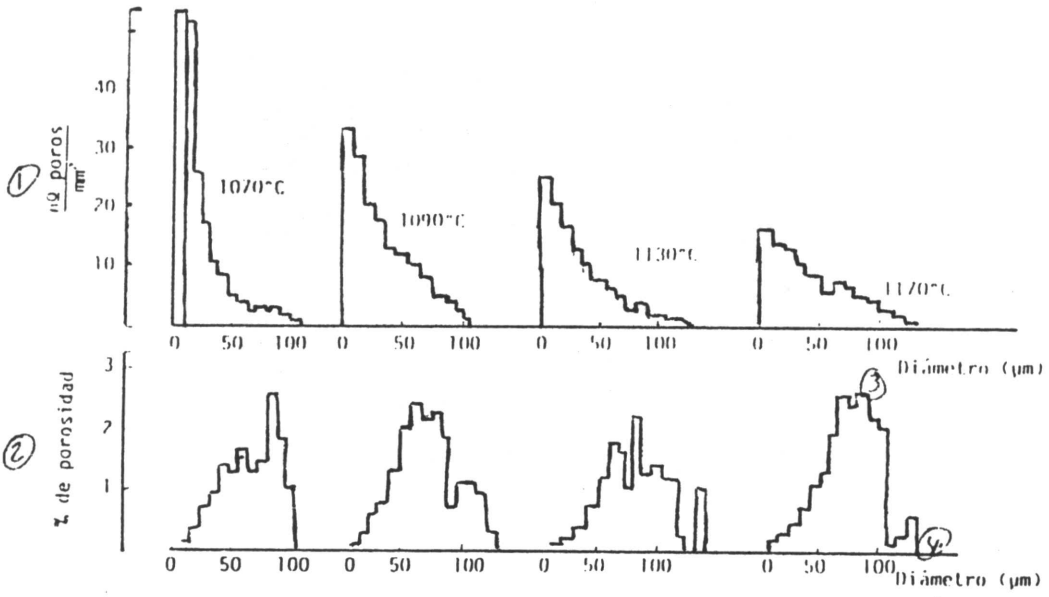


Figure 13.- Microphotography of glaze 1 fired at 1150°C.

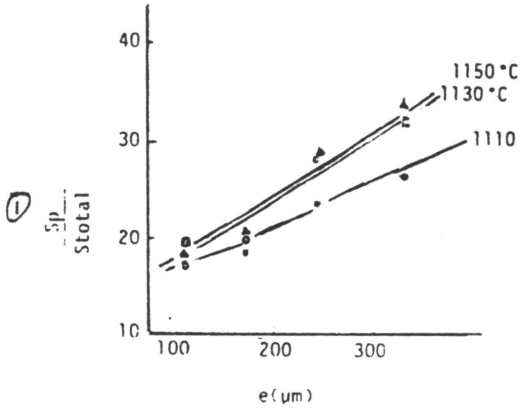


1) No. of pores mm2
2) Sp/St 3) Dv (µm)
4) Temperature (°C)

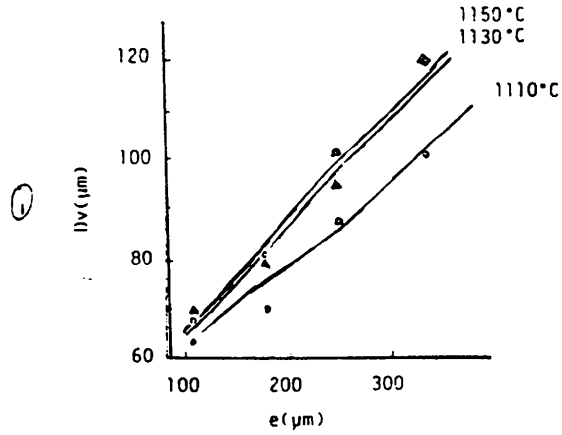
Figure 14.- Variation of no. of pores, porosity and average pore size with firing temperature of the glaze.



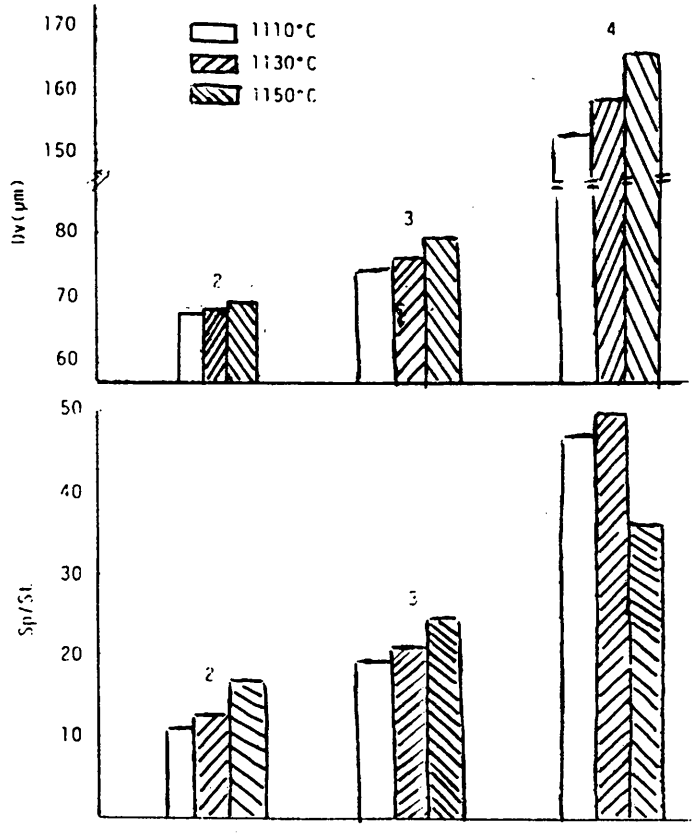
1) No. of pores mm2
2) % porosity
3) Diameter (µm)
4) Diameter (µm) 5) Figure 15.- Variation of pore size distribution with firing temperature.



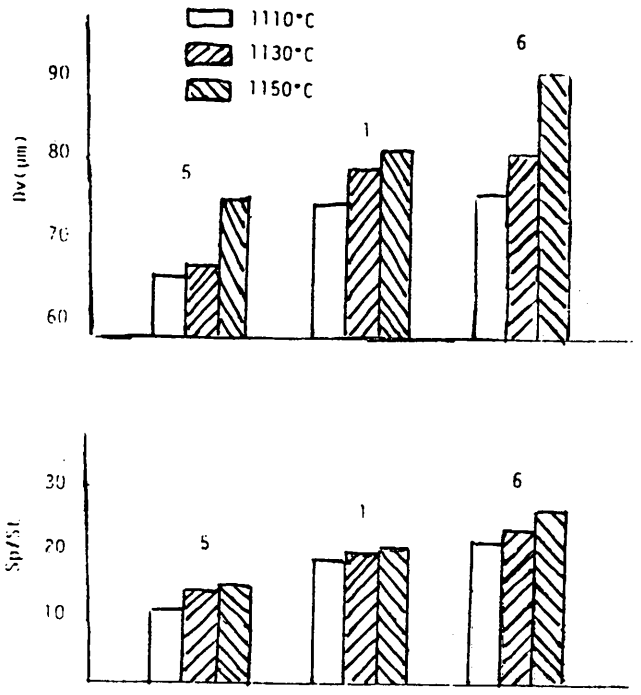
1) Sp S total
Figure 16.- Influence of glaze thickness on resulting porosity.



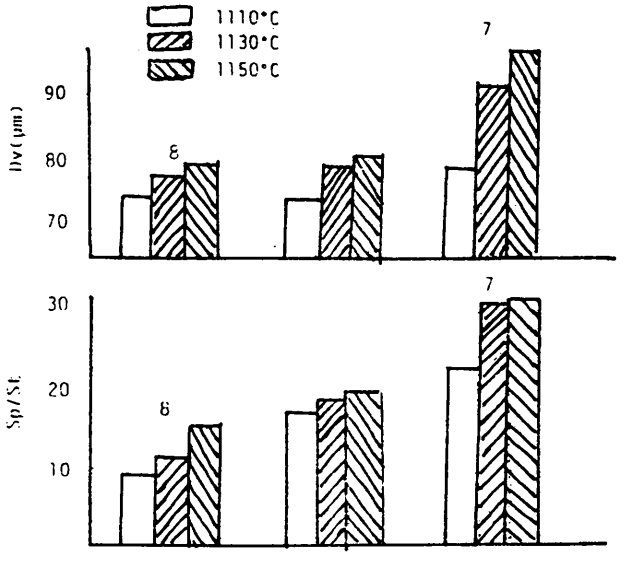
1) Dv (µm)
2) Figure 17.- Influence of glaze thickness on average pore size.



1) Figure 18.- Influence of nature of the fritted material on porosity and average pore size of the glaze (compositions 2, 3 and 4).



1) Figure 19.- Influence of nature of the fritted material on porosity and average pore size of the glaze (compositions 1, 5 and 6).



1) Figure 20.- Influence of fritted material content on porosity and average pore size of the glaze.

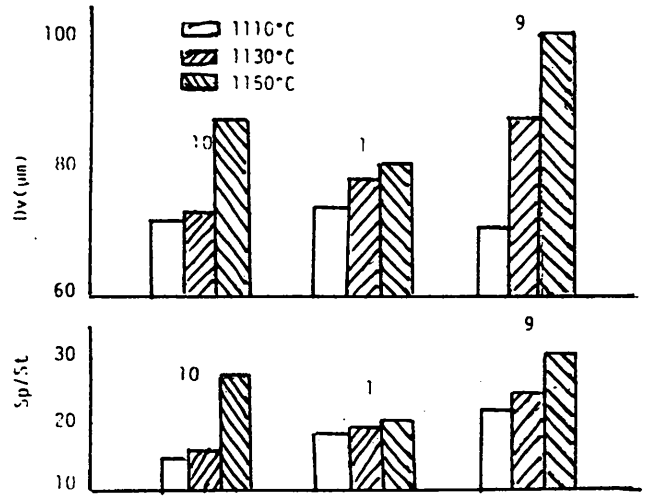


Figure 21.- Influence of zirconium silicate content on porosity and average pore size of the glaze.

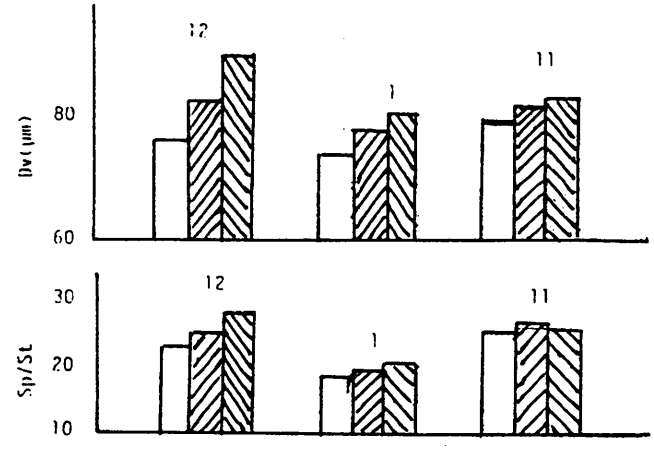


Figure 22.- Influence of nepheline content on porosity and average pore size of the glaze.

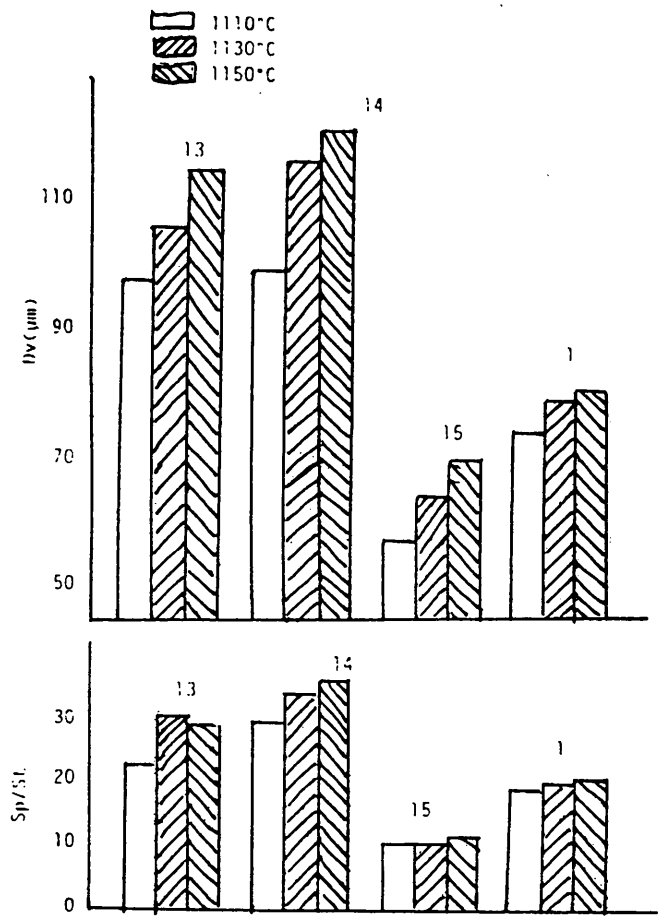


Figure 23.- Influence of content of some additives on porosity and average pore size of the glaze.

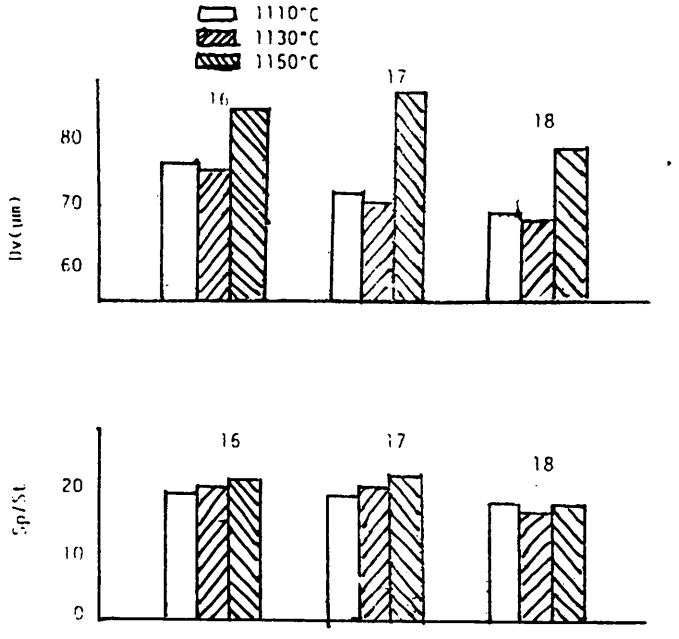


Figure 24.- Influence of the granulometric distribution of quartz on the porosity and average pore size of the glaze.

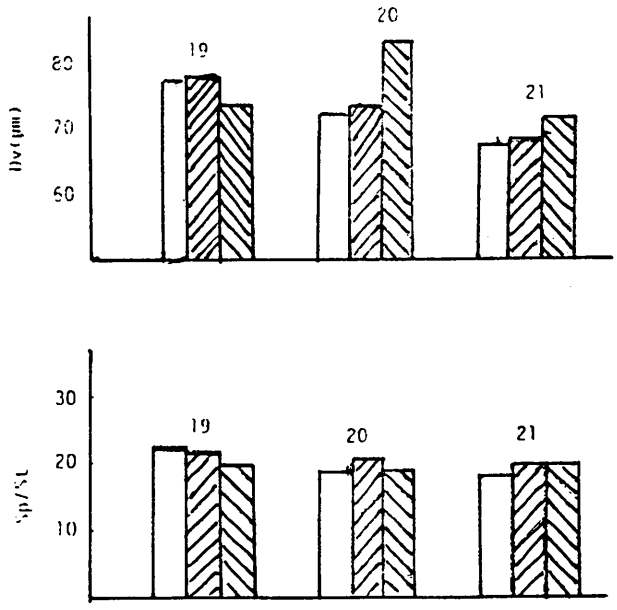


Figure 25.- Influence of the granulometric distribution of corundum on the porosity and average pore size of the glaze.

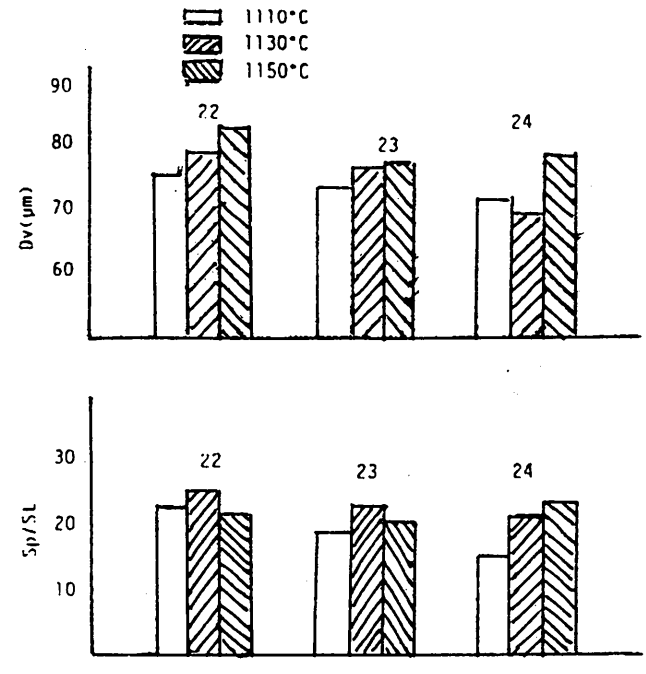


Figure 26.- Influence of the granulometric distribution of CaCO3 on the porosity and average pore size of the glaze.

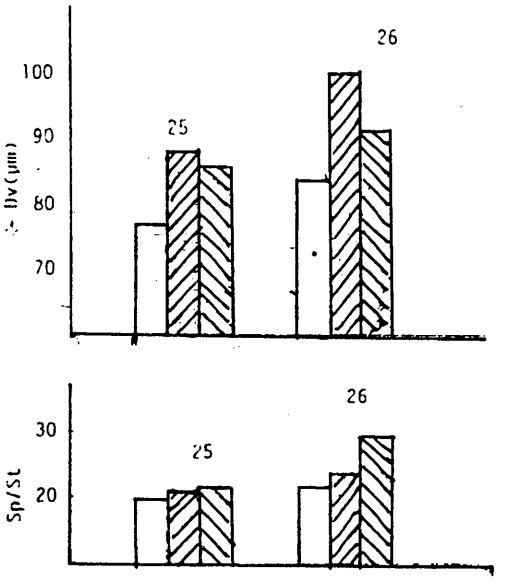


Figure 27.- Influence of the granulometric distribution of $ZrSiO_4$ on the porosity and average pore size of the glaze.