VITREOUS PORCELAIN. INFLUENCE OF PROCESS VARIABLES ON THE QUALITY OF THE FINISHED PRODUCT

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INTRODUCTION

The European Standards Committee (CEN), in its standard EN87 classifies ceramic paving and tiling into twelve groups, according to the type of mould used in their formation (pressing, extrusion, or casting) and according to their open porosity, measured by absorption of water (EN99). (1)

The type of mould generally used in the production of ceramic paving and tiling is dry pressing, although it should be mentioned that the term dry pressing is inappropriate, since the powder that is pressed has a humidity between 4 and 8%. Extrusion is preferably used for unglazed pieces and defines an area of products distinguished by their rustic decorative effects. The application of casting is almost insignificant, it is used for the preparation of some complementary pieces with complicated geometry.

In Spain, which is between the second and third largest producer of ceramic tiling and paving in the world, almost all of these products are glazed and 90% are moulded by dry pressing. Absorption of water in the tiles widely varies according to use; in those that are used for interior tiling, the absorption of water is usually over 14% (group III), on the other hand, in those used for paving and/or exterior paving and tiling, this property does not usually exceed 5% (groups BI and BIIa).

There is a wide range of ceramic paving and tiling products for innumerable applications. These tiles differ from each other not only in their format, size and colour, but also in their technical characteristics (physical, chemical, mechanical, etc.) Figure 1.

Public or industrial environments require paving with a high resistance to abrasion and a generally high mechanical resistance, the same is true for pavements used outside, these must have a high resistance to abrasion, since in the surrounding area there may be sand or other types of particles that will act as an abrasive on the ceramic material, encouraging wear.

The most common glazed ceramic paving (groups BI and BIIa) do not usually fulfil the technical characteristic requirements for these applications, as a result it was necessary to prepare a ceramic product that integrated these properties.

The term vitreous porcelain is used to designate a particular type of ceramic paving and tiling. Vitreous porcelain is an unglazed, homogeneous material, with a very low absorption of water, normally less than 0.1%, which indicates high compaction of the product during pressing and good technical performance. (2).

PHYSICAL PROPERTIES		GROUP BI EN 176	GROUP BIIA EN 177	GROUP BIIIC EN 178	GROUP BIII EN 159
EN 99	Absorption of water (% weight) Av. value	≤ 3	3 < E ≤ 6	6 < E ≤ 10	> 10
		≤ 3.3	≤ 6.6	≤ 11	
EN 100	Rupture modulus (N/mm^2) Av. value	≥ 27	≥ 22	≥ 18	≥15 esp. ≥7.5 mm. ≥12 esp ≥7.5 mm.
		–	≥ 20	≥ 16	
EN101	Mohs Hardness Test a) Glazed tiles >3 tiling b) Unglazed tiles >5 paving	≥ 5 ≥ 6	≥ 5 ≥ 6	≥ 5 ≥ 6	≥ 3 revest. ≥5 pavim.
EN 102	Resist. to deep abrasion. Unglazed tiles Max. vol. abrasioned in mm3	≤ 205	≤ 345	≤ 540	–
EN 154	Resist. to surface abrasion. Unglazed tiles Abrasion types I-IV	*	*	*	*
EN 103	Lineal dilation co-eff. from 25-100oC (x 10-6K-1)	≤ 9	≤ 9	≤ 9	≤ 9
EN 104	Resistance to thermic shock	–	–	–	–
EN 105	Resistance to crazing Glazed tiles	–	–	–	–
EN 155	Expansion through humidity Unglazed tiles (mm/m)	–	–	≤ 0.6	–
EN 202	Resistance to freezing.	–	–	–	–

Fig. 1 PHYSICAL PROPERTIES OF CERAMIC PAVING AND TILING.

Porosity has a considerable influence on technical characteristics, mainly on mechanical characteristics (rupture modulus) and surface characteristics (resistance to abrasion, resistance to stains, resistance to chemical agents).

In some cases these technical characteristics limit use or are the cause of complaints, moreover, if the open porosity is formed by large size pores, the closed porosity will be greater, since the surface, due to the orientation of the clayey particles during moulding, always has a much lower porosity than the interior of the piece, and this gives two sources of problems. (3)

One of these comes from the presence of closed porosity, if the closed porosity is significant, it indicates that either the compactness of the unfired piece, or the composition of the mixture, or the pressing compression was deficient. If the compaction of the piece is deficient, contraction during firing will be greater and pyroplastic deformation will increase, as will the difference in compaction within the piece and between the various pieces, this can cause asymmetries and different sized pieces (calibres).

The other source of problems appears in polished vitreous porcelain products, which have a significant closed porosity. When the fired piece is polished the surface is abrasioned and the interior of the piece is left exposed, this can reduce resistance to stains and abrasion.

This investigation consisted of the study of the relationships between pressing variables (granulometric distribution, humidity and pressing pressure) and the characteristics acquired by the unfired and fired piece, with the object of defining optimum operation intervals for process variables and discovering relationships that define the characteristics of the finished product as a function of process variables.

As mentioned above, the stability of dimensions and correct geometry (orthogonality, planarity, etc.) of the fired pieces are requisites that the finished products must fulfil.

The lack of dimensional stability of fired ceramic pieces, that manifests itself in different calibres or sizes, is generally due to the pieces undergoing different lineal contraction during firing. On the other hand, asymmetries (lack of orthogonality in the piece) are a consequence of unequal contraction in different parts of the same piece during firing. In both cases, the lineal contraction differences are caused by a lack of uniformity in the porosity of the unfired pieces, whether within pieces or between pieces, and/or by inequalities in firing temperature. Lack of planarity can be due to pyroplastic deformations, as well as to the causes mentioned above.

In order to avoid these defects, it is necessary to ensure that the (unfired) compaction of the pressed pieces (within and between pieces) is uniform and that the composition of the material used to prepare the piece fulfils the following requisites:

a) It must possess a sufficiently wide firing interval for the variations of lineal contraction, which can take place within or between pieces as a consequence of the alterations of temperature of firing that inevitably appear in the process, to be sufficiently reduced so that they do not cause appreciable differences in size (different calibres) or in shape (asymmetries, lack of planarity, etc.)

b) It must provide the piece, in the firing temperature interval, with the physical properties required (water absorption, mechanical resistance, etc.) without pyroplastic deformations appearing. The pyroplastic index (P.I.) of the composition must be sufficiently low to prevent external forces, to which the pieces are submitted during firing (blows, force of gravity, etc.), causing defects due to lack of planarity in the finished product.

c) Excessively high firing temperatures should be avoided, in order to reduce energy consumption, where possible, during the firing stage.

FIRING INTERVAL

In the firing of vitreous porcelain ceramic products, vitrification or sintering, in the presence of a liquid phase, is the process of densification that generally serves to reduce the porosity of fired pieces and give them the required properties. During firing of these products a viscous vitreous phase develops which surrounds the most refractory particles and which under surface tension forces, that are generated in the fine pores of the piece, tends to approach the particles, increasing their contraction and reducing their porosity. Similarly, as the vitrification develops, the material stops behaving like a rigid solid, due to the liquid phase present, and when a stress is applied (gravity forces, for example) a permanent deformation, known as a pyroplastic deformation, may be produced. (4)

As for the preparation conditions of the pieces (similar composition, pressing variables, etc), the evolution of water absorption, lineal contraction and pyroplastic deformation depends fundamentally on the quantity of the liquid in the liquid phase formed, its viscosity, its variation with temperature and the size of its constituent particles.

For the composition to possess an appropriate interval, or a sufficiently wide interval not to produce the aforementioned defects, and for the piece to attain the required characteristics (porosity, mechanical resistance, etc.), it is essential that the following requisites are fulfilled.

1) During firing, a sufficient quantity of liquid phase of appropriate viscosity must be developed in order for the piece to reach the porosity required (<0.2%) without being deformed.

2) In the firing interval, the variation of liquid phase content and/or viscosity with temperature must be gradual, so that the alterations in lineal contraction, water absorption and pyroplastic deformation are also gradual.

The evolution of the different components of the paste, both clayey and non-clayey, has been widely studied and the type of response of different mineralogical species and mixtures is known.

ADAPTATION TO RAPID SINGLE FIRING PROCESS

To aid the internal oxidation of the pieces and hence, to avoid black heart, the use of clays containing organic material, sulphurs, etc., even in small proportions, must be avoided in the raw material.

SUITABILITY FOR UNFIRED PROCESSING

Besides the aforementioned requisites that the composition must fulfil, so that it behaves suitably during firing and gives the finished product the characteristic properties required, it must also fulfil other requirements regarding its correct processing before firing. The plastic/detergent ratio and the size of particle must be carefully balanced in the composition of the material so that the aqueous suspension is easily deflocculable, so that the resulting powder can be adequately moulded and the drying of the moulded piece can be carried out without difficulty, and so that the unfired piece possesses a sufficient mechanical resistance for pressing.

AVAILABILITY OF RAW MATERIALS

The clays, feldspars, and feldspathic sands selected for the composition of the pastes fulfill all the requisites above. As the ceramic product concerned has technical characteristics which allow for high efficiency and as it is an unglazed product, the cost of the raw materials is not a limiting factor as in other ceramic products, thus a choice can be made from national or imported raw materials.

CHARACTERIZATION OF THE PASTE

To carry out this study an industrial paste made from white clays containing illite, kaolinite, sodium feldspar, potassium feldspar and feldspathic sand was used.

The tests carried out to characterize this industrial paste were as follows:

Residue at 63 u: 1.1%
Slip screen: 125um
Pressing pressure: 400kg/cm3
Pressing humidity: 5.5%
Apparent dry density: 1.993 g/cm3

Temperature (oC)	Contraction Lineal (%)	Absorption Water (%)	Densit Apparent (g/cm3)
1180	7.4	0.31	2.380
1200	7.7	0.01	2.411
1220	7.7	0.00	2.419

These tests show the good behaviour of the paste chosen, during pressing (apparent dry density) and firing (Lineal contraction, water absorbtion and apparent density after firing).

PHYSICAL CHARACTERIZATION OF PARTICLES AND AGGLOMERATES

To carry out this part of the study the formulated paste was departed from, the slip was prepared and drying by industrial atomization was carried out.

The characterization involved the determination of:

- Distribution of the primary particle sizes. - Granulometric distribution of agglomerates resulting from damp milling and subsequent spray drying - Morphology and microstructure of agglomerates obtained (granules). - Apparent density of agglomerates obtained from drying by atomization. - Apparent density of agglomerate layer (pressing powder). - Fluid velocity and Hausner Index for the different granulometric fractions.

GRANULOMETRIC DISTRIBUTION OF PRIMARY PARTICLES

Table I shows the residues obtained from screening the particles resulting from the damp industrial milling of the paste used in the study.

TABLE 1

Screening residues accumulated from particles resulting from damp milling.

Mesh Aperture (μm)	Residue (%)
125	< 0.01
60	< 0.01
50	0.50
40	1.50

The granulometric distribution of particles smaller than 40um, determined by Serigraph, is given in Figure 2.

GRANULOMETRIC DISTRIBUTION OF AGGLOMERATES RESULTING FROM DAMP MILLING AND SUBSEQUENT SPRAY DRYING

The results obtained are shown in Table II.

TABLE II

Size distribution of powder agglomerates resulting from damp milling and subsequent spray drying .

Mesh Aperture (µm)	Accumulated sifts (%)
750	99.8
500	96.3
400	77.7
300	52.4
200	30.4
125	5.5
80	1.0

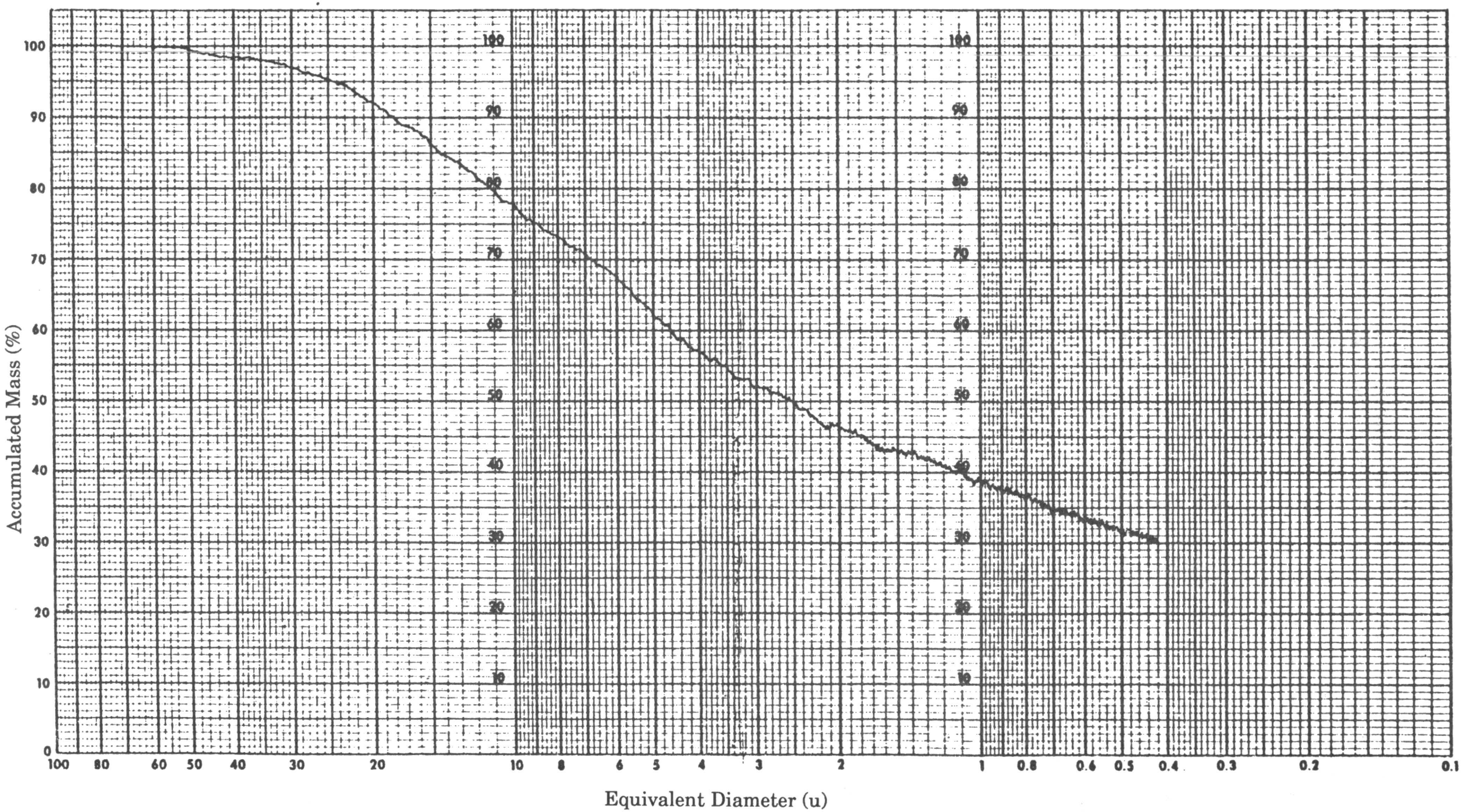


Figure 2 Distribution of particle size in vitreous porcelain paste.

Figure 3 shows these results in the form of a frequency histogram, to emphasise the predominant granulometric fractions. As can be seen, almost all the powder atomized has a granule size between 125 and 500 µm.

MORPHOLOGY AND MICROSTRUCTURE OF PARTICLE AGGLOMERATES (GRANULES)

The shape and texture of the agglomerates used in this study were determined through a scanning electron microscope. In Figures 4, 5, and 6 microphotographs corresponding to the most representative granulometric fractions are shown.

A greater sphericalness and lesser rugosity can be seen on the surface of the granules when their size is reduced. In larger sized fractions (over 400 um) the surface is much more rugged and much less spherical, mainly due to the fact that during the spraying operation the finer granules stick to the surface of the larger sized granules. This phenomenon is notably exaggerated in the 500- 750 um fraction, where the form of the agglomerates is very irregular.

APPARENT DENSITY OF AGGLOMERATES OBTAINED FROM SPRAY DRYING

The apparent density of agglomerates prepared by spraying was calculated indirectly from the density of the agglomerate layer compacted through vibration (t). This method is based on the proven fact that the intergranular porosity of a layer of similar sized granules, compacted by vibration, is 40 % (identical to that obtained in the compacting of monodimensional sphere). Consequently, the apparent density of the granules (ρ_G) can be calculated dividing the apparent density of the compacted layer ($\rho t_{) \text{ by } 0,6. (6)}$

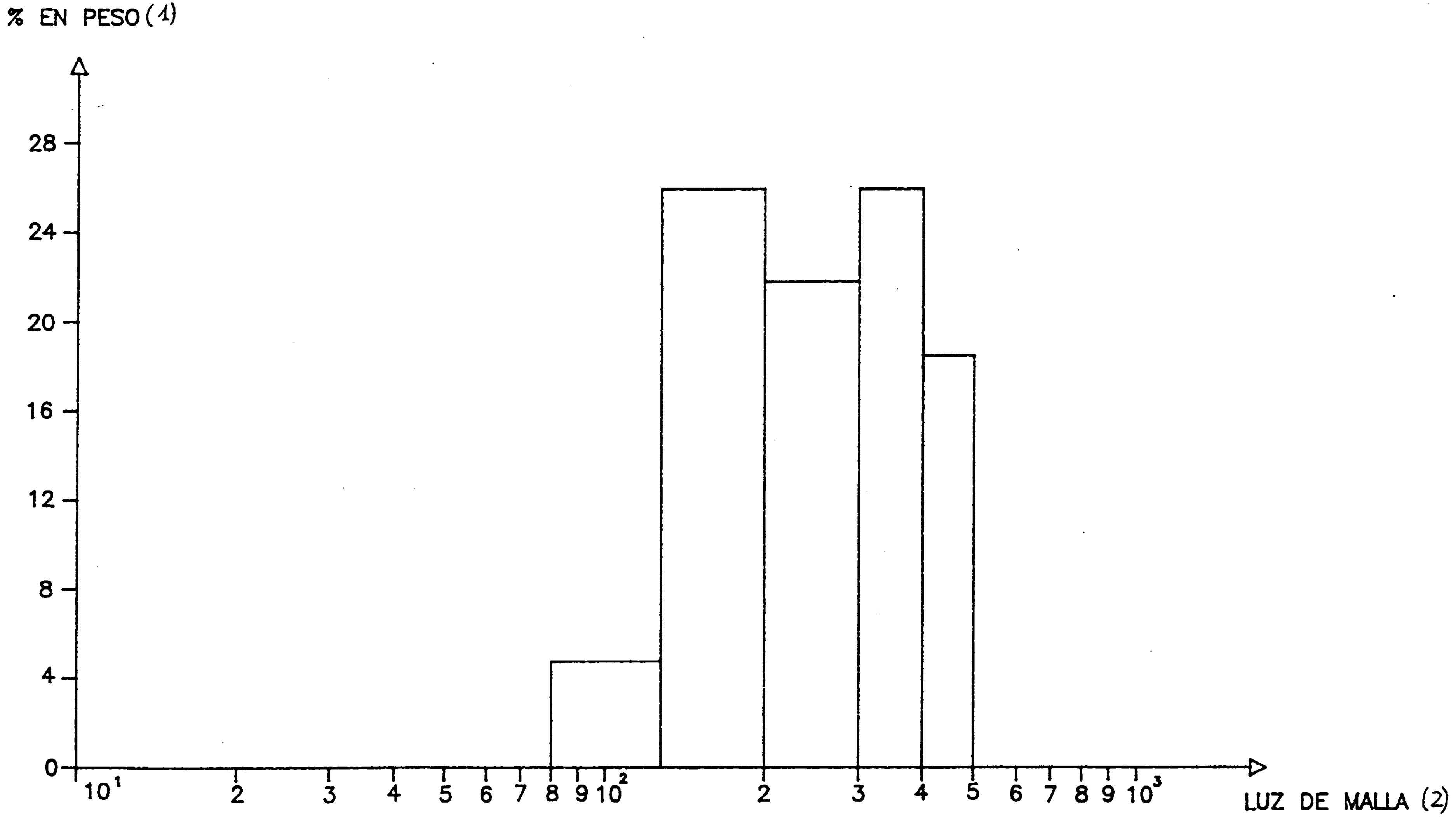


Figure 3. Frequency histogram of the size distribution of agglomerates

(1) % In Weight

(2) Mesh Aperture.

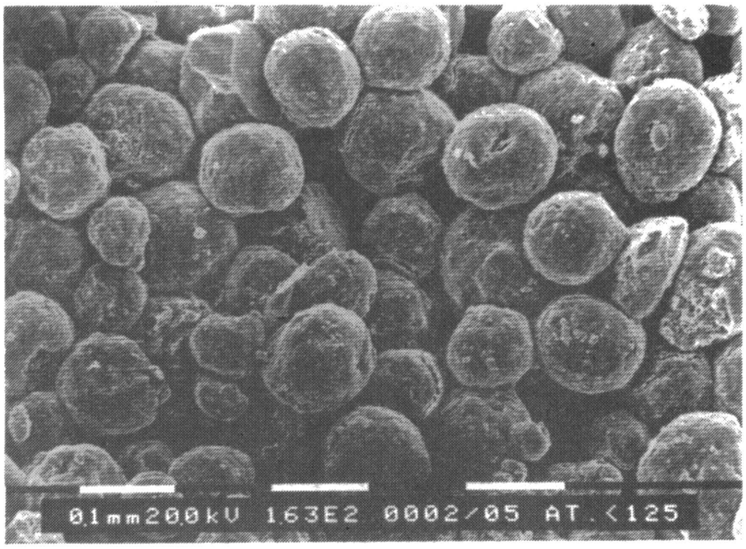


Figure 4 Microphotograph of the 80-125um fraction

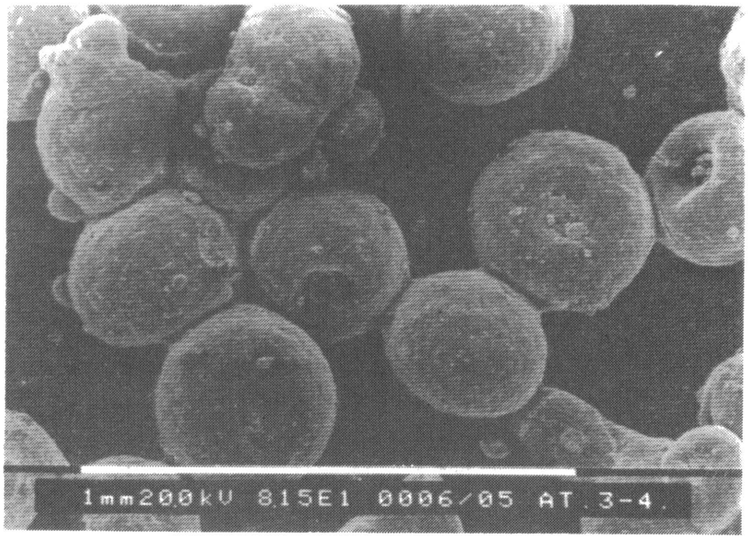


Figure 5 Microphotograph of the 300-500um fraction

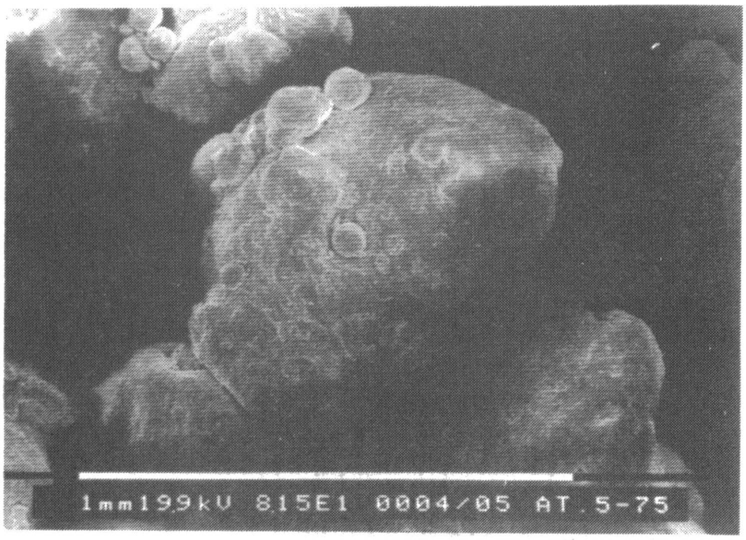


Figure 6 Microphotograph of fraction greater than 500um

In Table III, the apparent densities of the granules (ρ_G) of the different sized fractions corresponding to the agglomerates prepared are given.

TABLE III

Values of ρ_G for different fractions of agglomerates prepared by spraying.

Granulommetric Fraction (um)	Density ρ_G (g/cm3)
80-125	1.843
200-300	1.778
400-500	1.747

The apparent densities of agglomerates larger than 500um cannot be calculated by this method, due to the fact that the granules have such an irregular form that the hypothesis of the intergranular porosity being 40% cannot be assumed.

As can be seen in Table III, the apparent density decreases as the size increases. This is probably due to the fact that, as the size of the agglomerate increases, the space occupied by internal craters and hollows in the granule also increases.

APPARENT DENSITY OF AGGLOMERATE LAYER (PRESSING POWDER)

Table IV shows the apparent densities (o) of the layer resulting from the simple pouring of the powder into the mould and from submitting the layer to vibration with subsequent compacting of the powder(ρt). The humidity content is also indicated.

TABLE IV

Apparent density of agglomerate layer

Humidity Content Xp (Kg water/Kg dry sol.)	ρ_o (g/cm^3)	ρ_t (g/cm^3)
0.025	1.010	1.167
0.050	1.029	1.174
0.075	1.014	1.189

It can be seen that the highest apparent density value for the layer obtained by pouring corresponds to the spray with a humidity content Xρ = 0.050. This is probably due to the fact that, in the case of the most humid spray, the water content is excessively high and attractive forces between the granules appear due to the presence of the liquid on the surface, and, in the case of the spray with a humidity content Xp = 0.025, the low humidity can produce breaks in the granules, less fluidity and thus lesser density.

With regard to the apparent density obtained by vibration, an increase is noted with increase in humidity content. This is due to the attractive forces being overcome by the vibration, thus the final compacting is similar for the three cases tested. However the progressive increase in humidity content is reflected in the values of the apparent density calculated as the ratio between the mass of powder and the volume it occupies.

FLUID VELOCITY AND HAUSNER INDEX OF THE DIFFERENT GRANULOMETRIC FRACTIONS OF AGGLOMERATES OBTAINED

Table V gives details of the fluid velocity and Hausner Index for granulometric fractions corresponding to large, medium and fine sized granules (6).

TABLE V

Fluidity of agglomerates

Granulometric Fraction	Fluid Velocity cm^3/s)	Hausner Index (ρ_t / ρ_o)
80-125 μm	24.3	1.162
200-300 μm	25.7	1.151
400-500 μm	23.8	1.173

The following conclusions can be made from the results:

1) The fraction between 80-125 um has a lesser fluidity than the 200-300 um fraction. This is because, in spite of the fine granule being more dense, its smaller size has a larger number of contacts between particles. Also in this fine fraction fragments of larger sized granules can be found that have been fractured during the process.

2) The fluidity of the large sized fraction (400-500 um) is less than that of the 200-300 um fraction. This is due to the low density of the granule and the lesser sphericalness of this with respect to the other fractions. In this fraction, granules formed by the union of smaller sized granules are found, these give rise to irregular forms such as have been seen in the microphotographs.

To determine the influence that the humidity exerts on fluidity, the value of these parameters was obtained for the agglomerates obtained with different humidity values. (Table VI).

TABLE VI

Influence of humidity on fluidity

Humidity Content (Kg water/kg dry sol.)	Fluid Velocity (cm^3/s)	Hausner Index
0.025	24.6	1.158
0.050	24.0	1.167
0.075	23.0	1.184

It is seen that the fluidity decreases as the humidity increases, which is noted both in the fluid velocity and the Hausner index.

PRESSING OF ATOMIZED POWDER. INFLUENCE OF PRESSING VARIABLES ON DEVELOPMENT OF THIS OPERATION AND ON THE PROPERTIES OF THE MOULDED PIECE

In the production of vitreous porcelain, the distribution of apparent density in the pressed piece and the distribution of porosity in the crude piece, are fundamental to the behaviour in the firing stage and to the technical characteristics of the fired piece.

To determine the effect that the pressing process variables (pressure and pressing humidity) have on apparent density and on the distribution of pores in the pressed piece, a set of samples were produced at different pressing pressure and humidity values. The values of pressing pressure were 150, 300 and 600 kg/cm3 and the values of humidity (Xp) used were 0.0250, 0.050 and 0.075 kg water/kg dry sol; this is the interval of values used in the production of vitreous porcelain. (7)

The ceramic powder compacting phase is also influenced by the state of agglomeration of the particles that compose the granules. The state of agglomeration is quantified by the following characteristics: hardness, granule size and density distribution,granule types, etc. According to the studies carried out, deformability decreases (hardness increases) as the density of the granule increases, which means that higher pressing pressures must be used than those used for softer granules, in order to obtain similar results.

To study the influence that the size and hardness of the agglomerates have on the porous structure of the dry piece, porosimetric distributions were determined by mercury porosimetry.

For each pressing humidity-pressure combination, six samples were moulded in order to reduce experimental error.

APPARENT DRY DENSITY

The most suitable procedure for characterizing the behaviour of pressing powder, during the compacting phase, involves determining the variation that the density of the compact powder layer undergoes (ρs) as pressing pressure P varies.

Figure 7 shows average values for apparent dry densities (s) as a function of the pressing pressure log at various values of pressing humidity corresponding to the three series of samples prepared at different pressing pressure (P) and humidity (Xp) values.

To analytically express the influence that these process variables have on the apparent dry density of the pressed piece, the property (ρs) has been related to pressing pressure by the equation:

$$\rho s = A + B \ln P$$

Table VII shows the values obtained for parameters A and B in this equation. These values were got by adjusting the values of figure 7 by lineal regression.

TABLE VII

Influence of humidity Xρ on the parameters A and B in the equation.

Xp (kg water/kg s. s.)	A (g/cm^3)	B (g/cm^3) (kg/cm^2)$^{-1}$	r^2
0.025	1.358	0.141	0.999
0.050	1.402	0.140	0.999
0.075	1.477	0.128	0.999

These results show how the pressing results have a marked effect on the apparent dry density of the moulded piece.

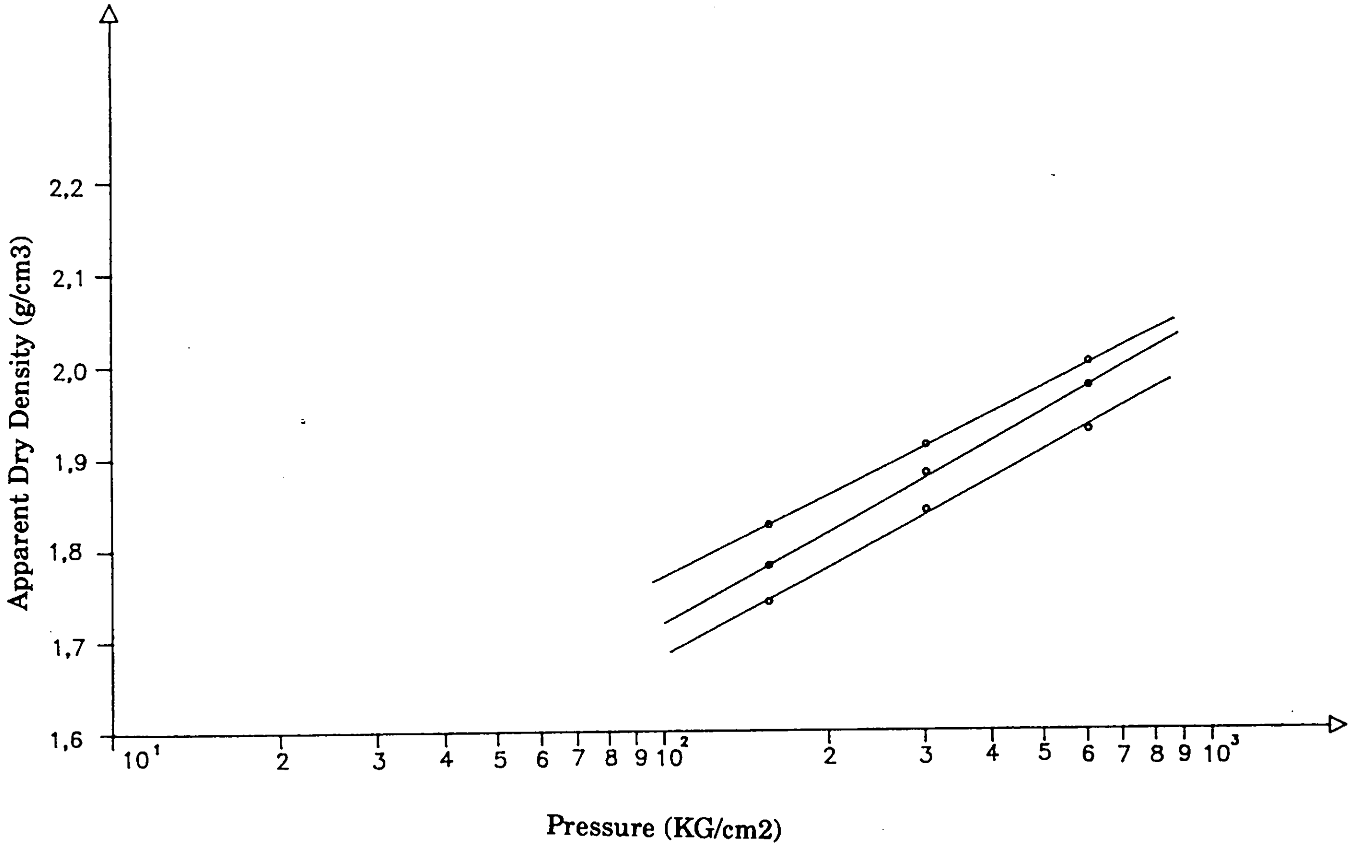


Figure 7.

VARIATION OF APPARENT DRY DENSITY WITH PRESSING PRESSURE AND HUMIDITY

In fact, as Xp increases, parameter A increases lineally and therefore, at constant pressure, so does the apparent dry density of the piece. On the other hand parameter B is decreased and hence the influence that pressure exerts on this property of the pressing piece also decreases.

SIZE DISTRIBUTION OF PORES

The size distribution of pores in samples pressed at pressing humidities of 0.025, 0.050 and 0.075 kg of water/kg dry solid and at pressures of 150, 300 and 600 kg/cm were determined by mercury porosimetry.

Figures 8, 9 and 10 show these porosimetric distributions, which correspond acceptably well to the function of the natural log distribution, as can be deduced from Figures 11, 12 and 13. These figures show the same results in the form of accumulated volume of the pores with diameter greater or equal to 2R on the probability scale plotted against 2R.

As can be seen in the interval of diameters between 75 and 0.01um, which corresponds to 90% of the pore volume (mesapores and macropores), the results are straight lines.

In Table VIII the average geometric values of the diameter are shown (2RG).

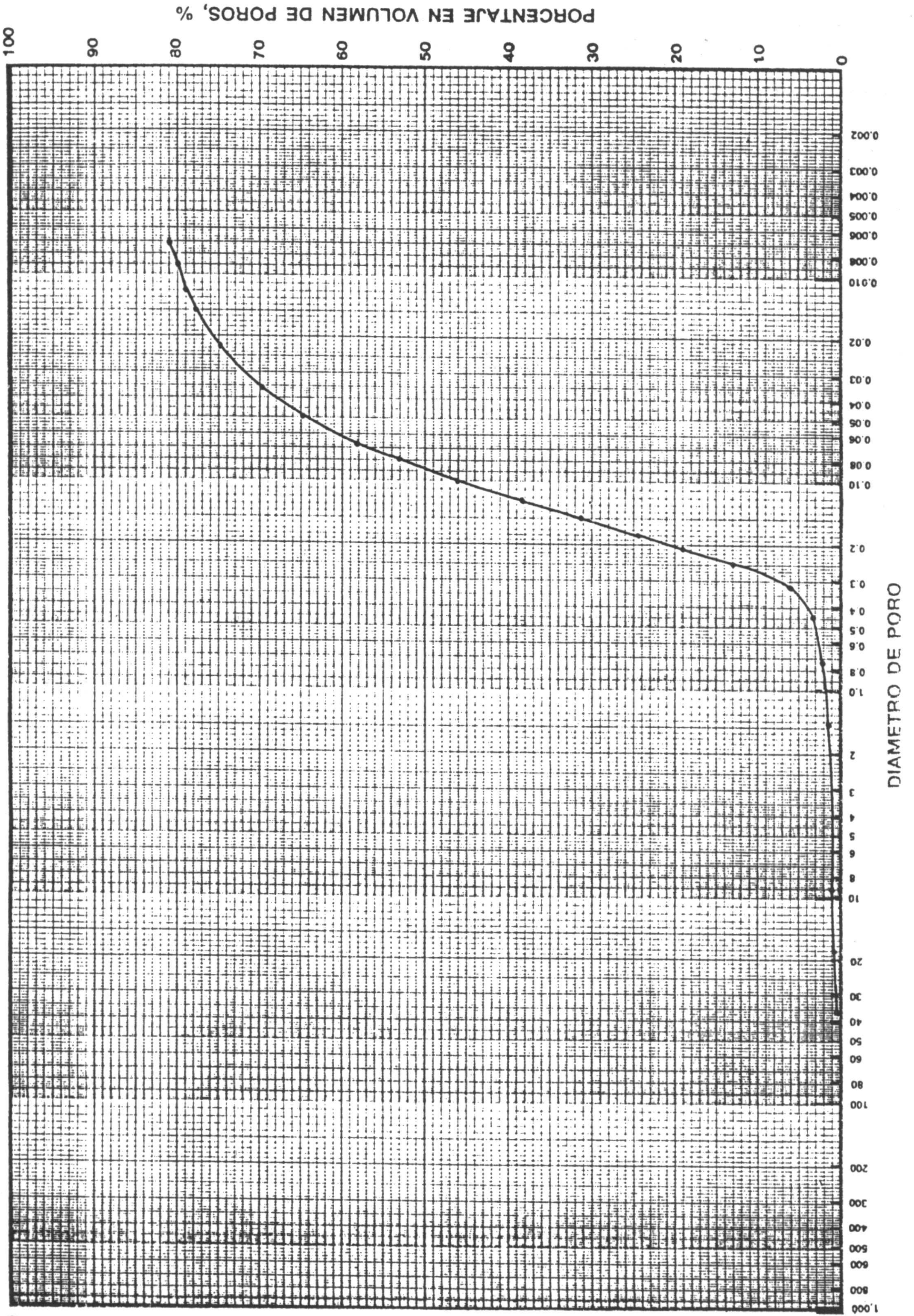


Figure 8. Size distribution of pores in dry piece. Pressing conditions: Pressure 300 Kg/cm2 Humidity 2.5%

Volume of accumulated intrusion (cc/g)
Percentage volume of pores %

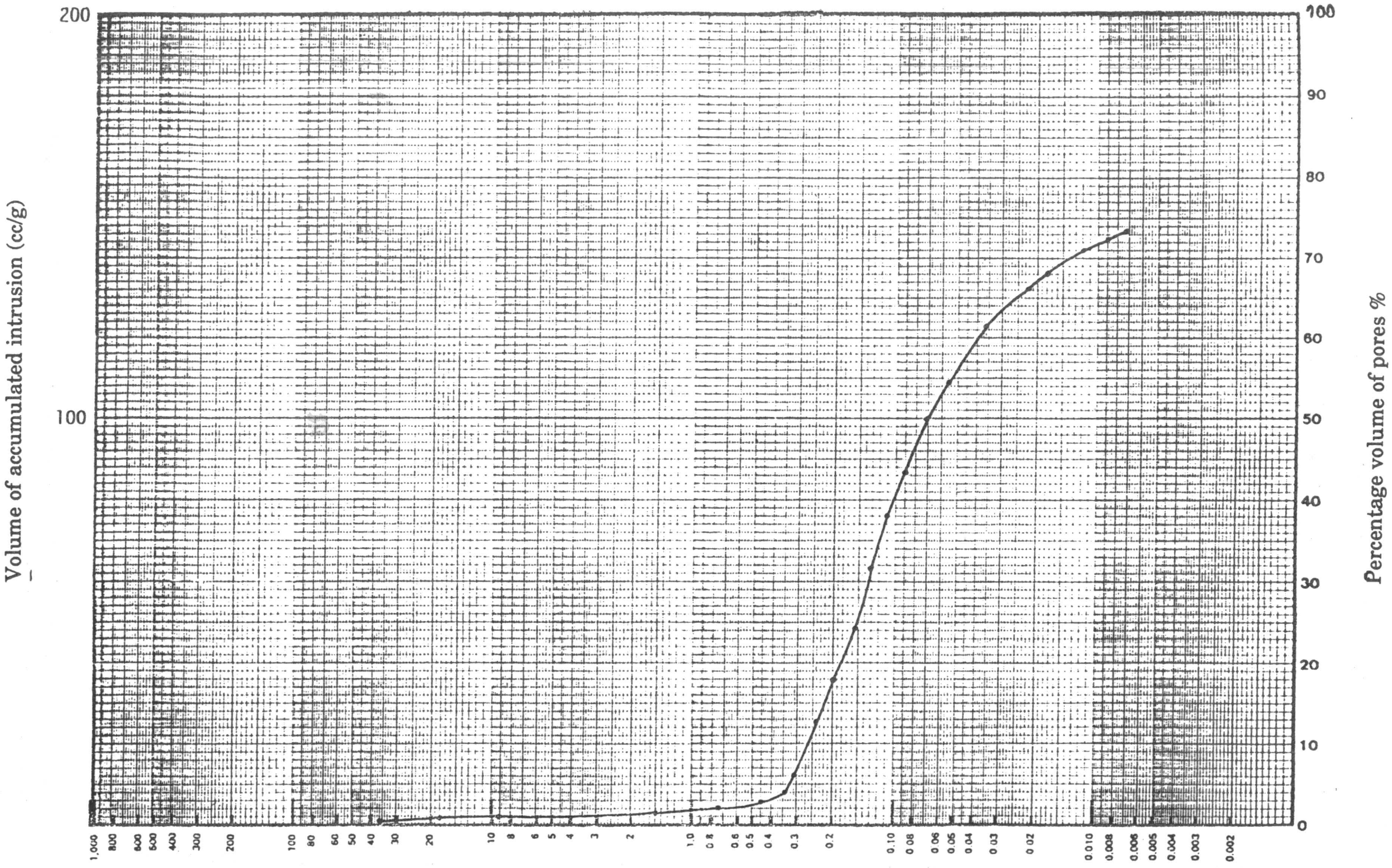


Figure 9.
Size distribution of pores in dry piece. Pressing conditions: Pressure 300 Kg/cm2 Humidity 5.0%

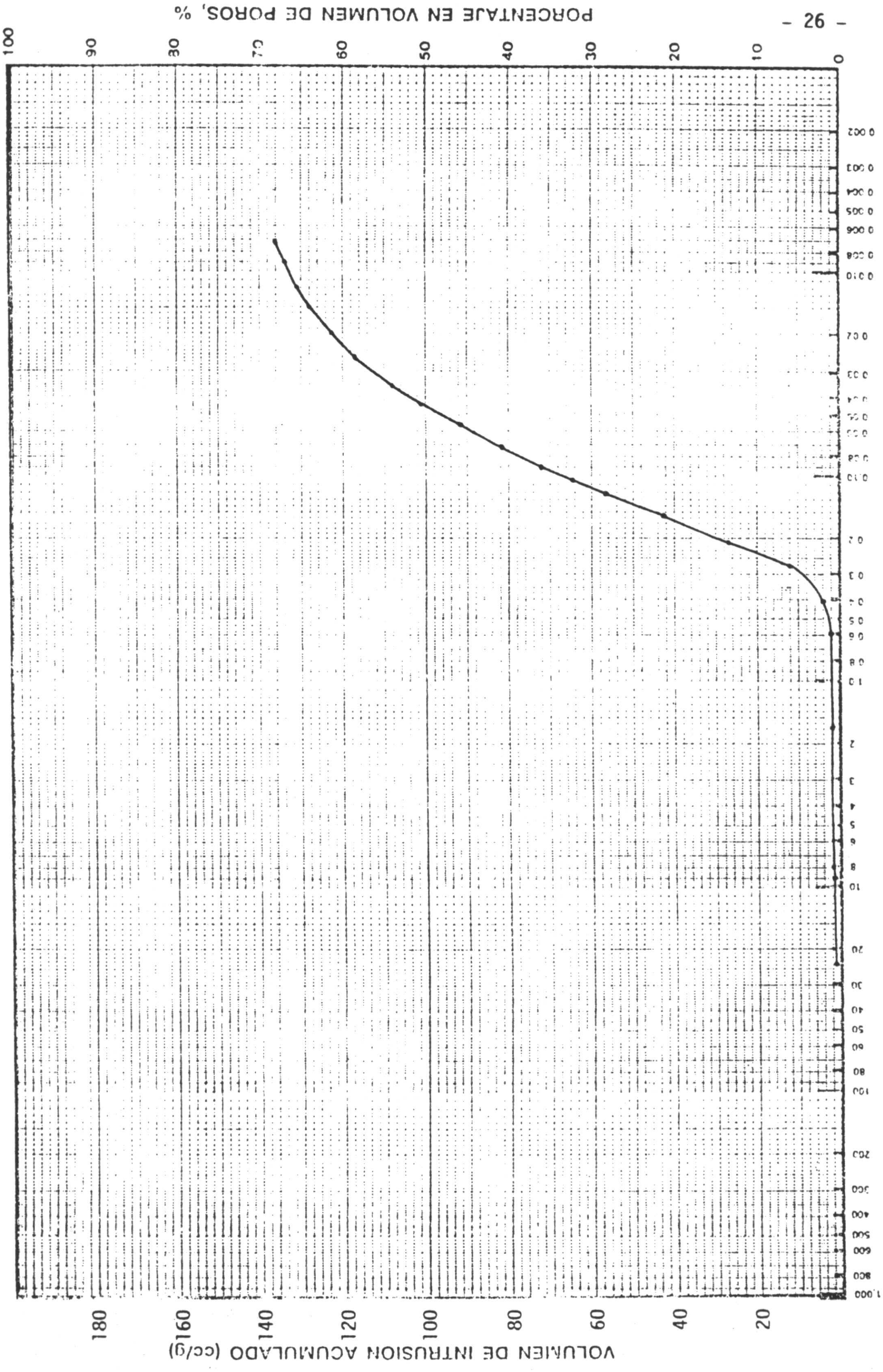


Figure 10.
Size distribution of pores in dry piece. Pressing conditions: Pressure 300 Kg/cm2 Humidity 7.5%
Volume of accumulated intrusion (cc/g)
Percentage volume of pores %

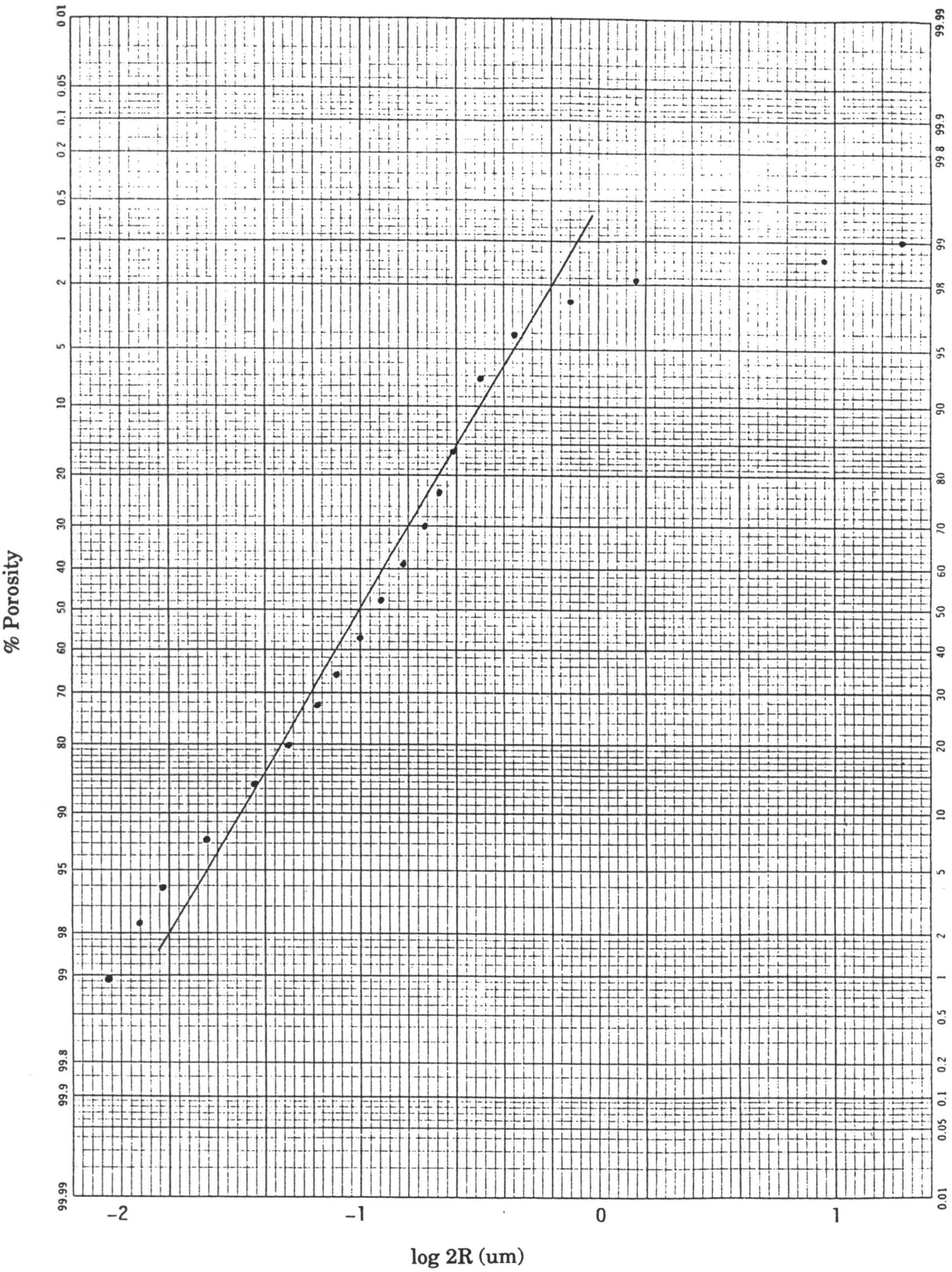


Figure 11.
Porosimetric distribution of crude pieces pressed at 300 kg/cm2 and at a humidity of 2.5%

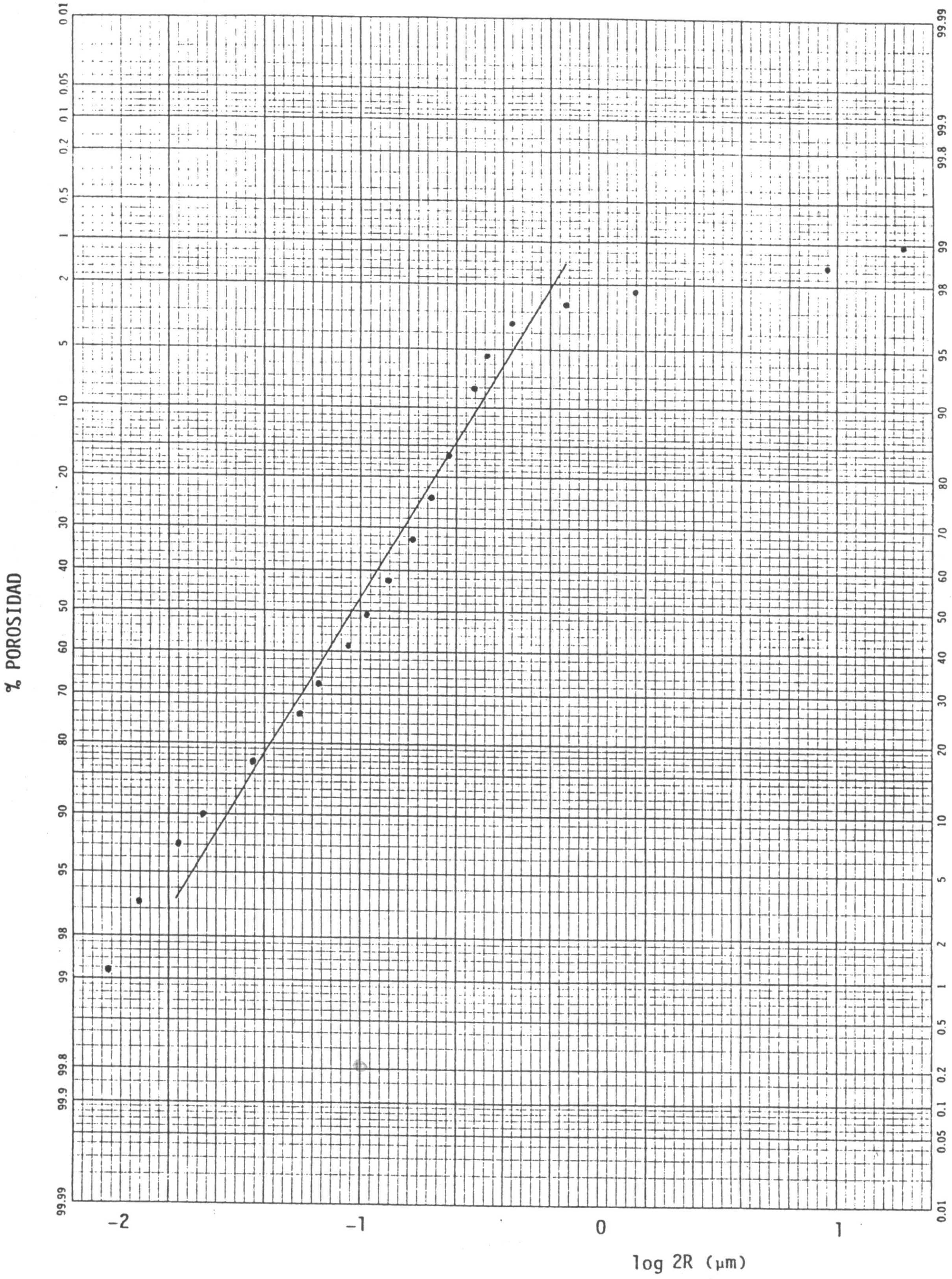


Figure 12.
Porosimetric distribution of crude pieces pressed at 300 kg/cm2 and at a humidity of 5.0%
% Porosity log 2R (um)

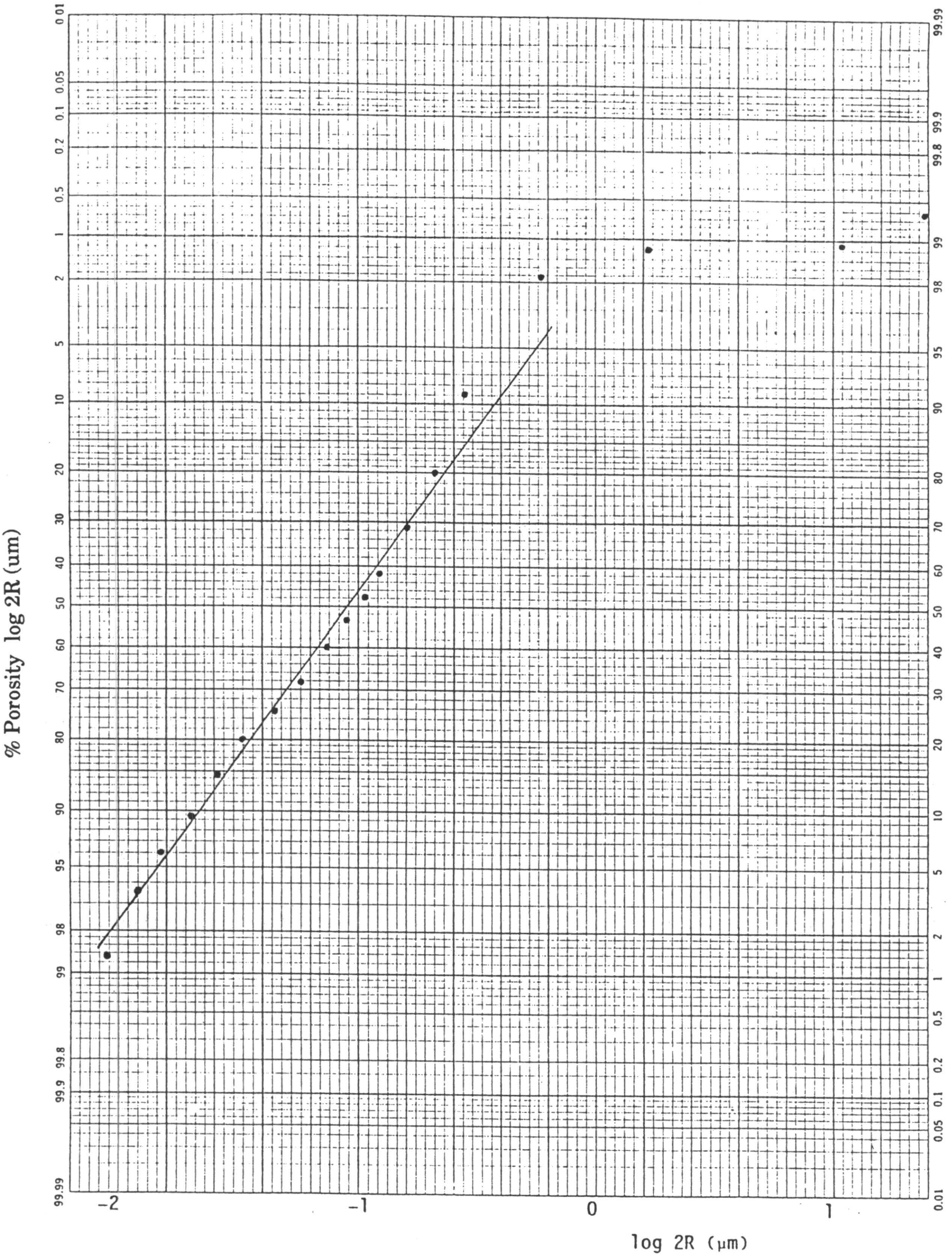


Figure 13.
Porosimetric distribution of crude pieces pressed at 300 kg/cm2 and at a humidity of 7.5%

TABLE VIII

Porosimetric distribution parameters of pressed pieces.

P (kg/cm^2)	Xρ (Kg water/kg dry solid)	$2R_G$
150	0.025	0.138
150	0.050	0.129
150	0.075	0.126
300	0.025	0.100
300	0.050	0.095
300	0.075	0.087
600	0.025	0.081
600	0.050	0.074
600	0.075	0.062

Figures 14 and 15 show the variation of average geometric diameter 2RG plotted against the pressing humidity content (xP) and against pressing pressure. As can be seen, the average geometric diameter decreases as the humidity content and pressure increase.

An examination of the results obtained reveals that:

- The average geometric diameter (2RG) of the pores in the pressing samples, at a pressing pressure (P), decreases as humidity increases (XP).

- The same tendency is seen in the pressed samples with a constant humidity content (Xp) as pressing pressure increases, i.e. the average geometric diameter decreases.

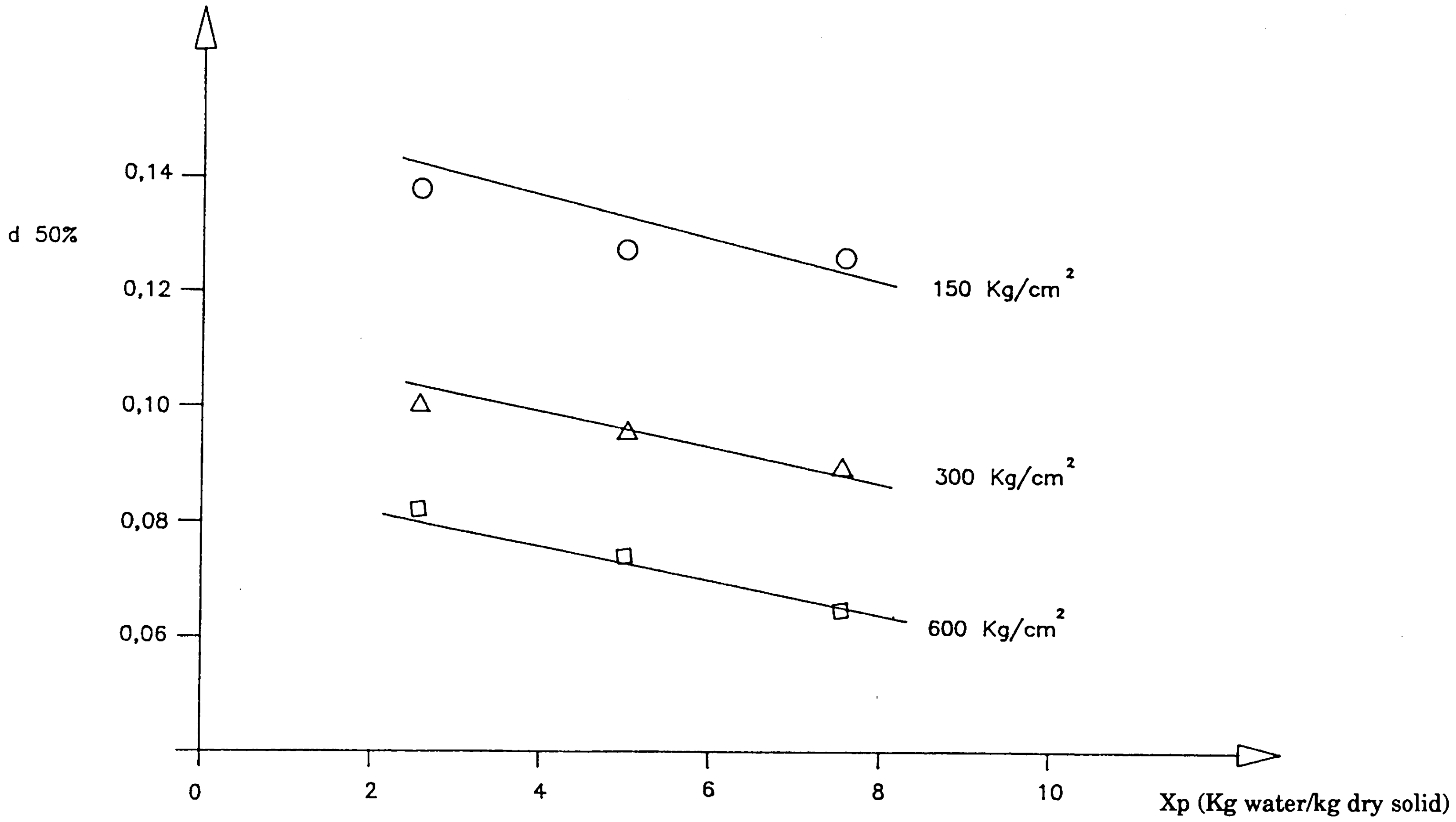


Figure 14.

VARIATION OF AVERAGE GEOMETRIC DIAMETER WITH PRESSING HUMIDITY

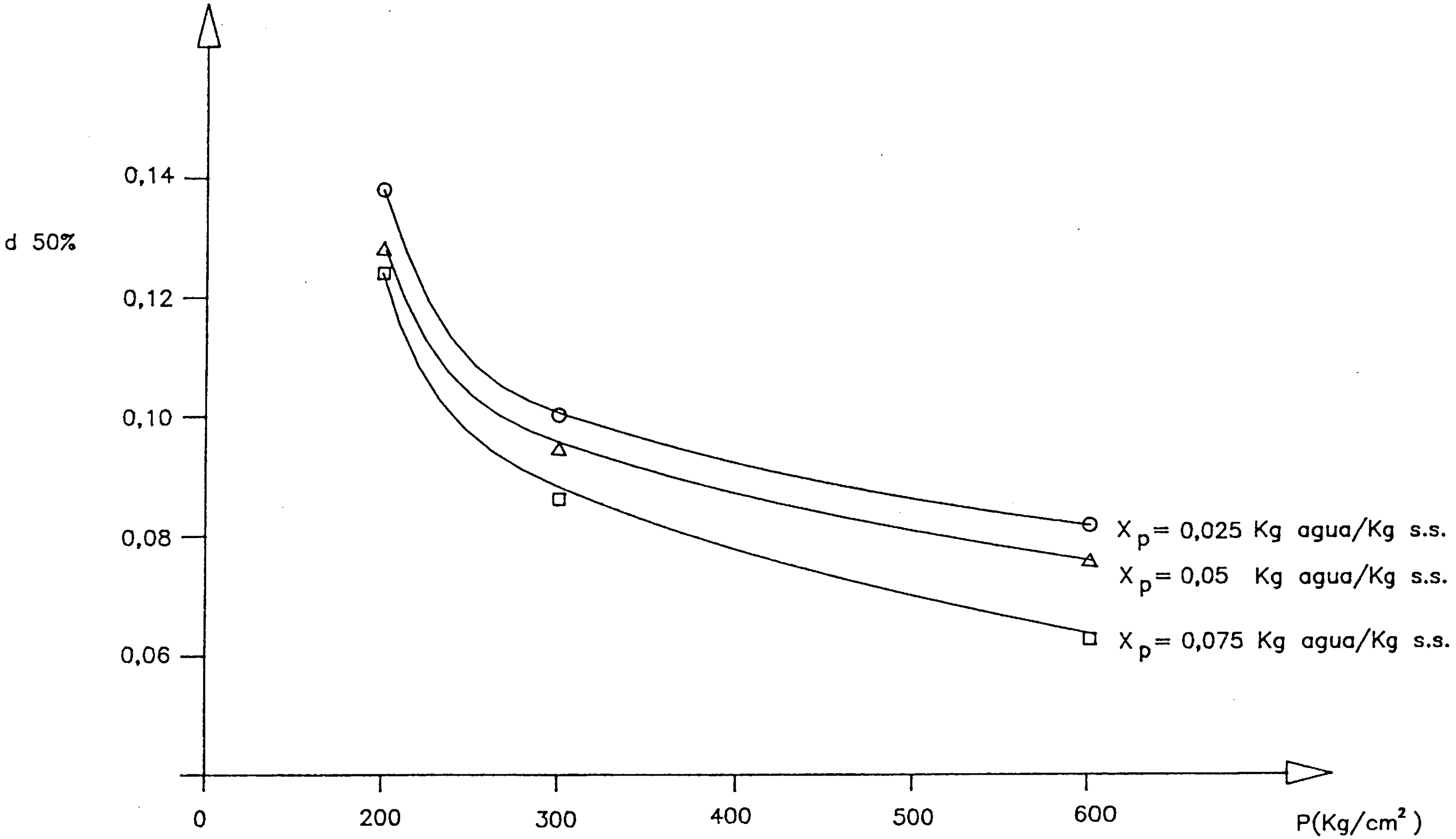


Figure 15.

VARIATION OF AVERAGE GEOMETRIC DIAMETER WITH PRESSING PRESSURE

Xp = 0.025 Kg water/Kg dry solid

FIRING OF PRESSED PIECES

Influence of pressing variables on behaviour of piece during firing process.

The lack of dimensional uniformity and the apparition of internal porosity in fired pieces are two of the most common, and worrying, defects in the production of vitreous porcelain. Since these defects arise from and/or are most influenced by the compaction of the crude pieces, the relationship between the apparent crude density and some properties of the fired piece was studied.(8) (9)

LINEAL CONTRACTION IN FIRING

The lack of dimensional uniformity between fired pieces or between different parts of the same piece is caused by difference in the compaction of the atomized powder in the pressing operation, and/or by variations in firing temperature.

To determine the effect that the degree of compaction and the firing temperature have on lineal contraction, 9 sets of samples were moulded. Within each series, the pressure and humidity values were altered. The pressing pressures (P) and the humidities(Xp) used are the same as those obtained in the compaction diagram. Each set contained fourteen samples, two for each one of the firing temperatures at which the tests were performed.

The samples, which were previously dried on a stove at 110°C, were fired at different temperatures at a heating rate of 25°C/min and remained at firing temperature for 6 mins. The lineal contraction during firing, expressed as the ratio of the difference in dimensions before and after firing with respect to the initial measurement, was determined for the fired pieces.

In figure 16 the values of apparent dry density (s) are plotted against lineal contraction during firing (S), for each firing temperature.

WATER ABSORPTION

To determine the effect of compaction and firing temperature on the open porosity of the fired pieces, measured as water absorption capacity (W), the pressed and fired pieces from the previous test were used.

Figure 17 shows the values of water absorbtion obtained for each pair of apparent dry density and firing temperature values.

APPARENT FIRED DENSITY

In figure 18, the apparent fired density values (ρc) of the samples corresponding to the nine sets prepared for the calculation of lineal contraction (S) and water absorption (W), in the form: Apparent fired density (ρC) plotted against apparent dry density (ρs) for different firing temperatures (T).

From the analysis of Figures 16, 17 and 18, the most significant effects of temperature on each one of the properties studied are the following:

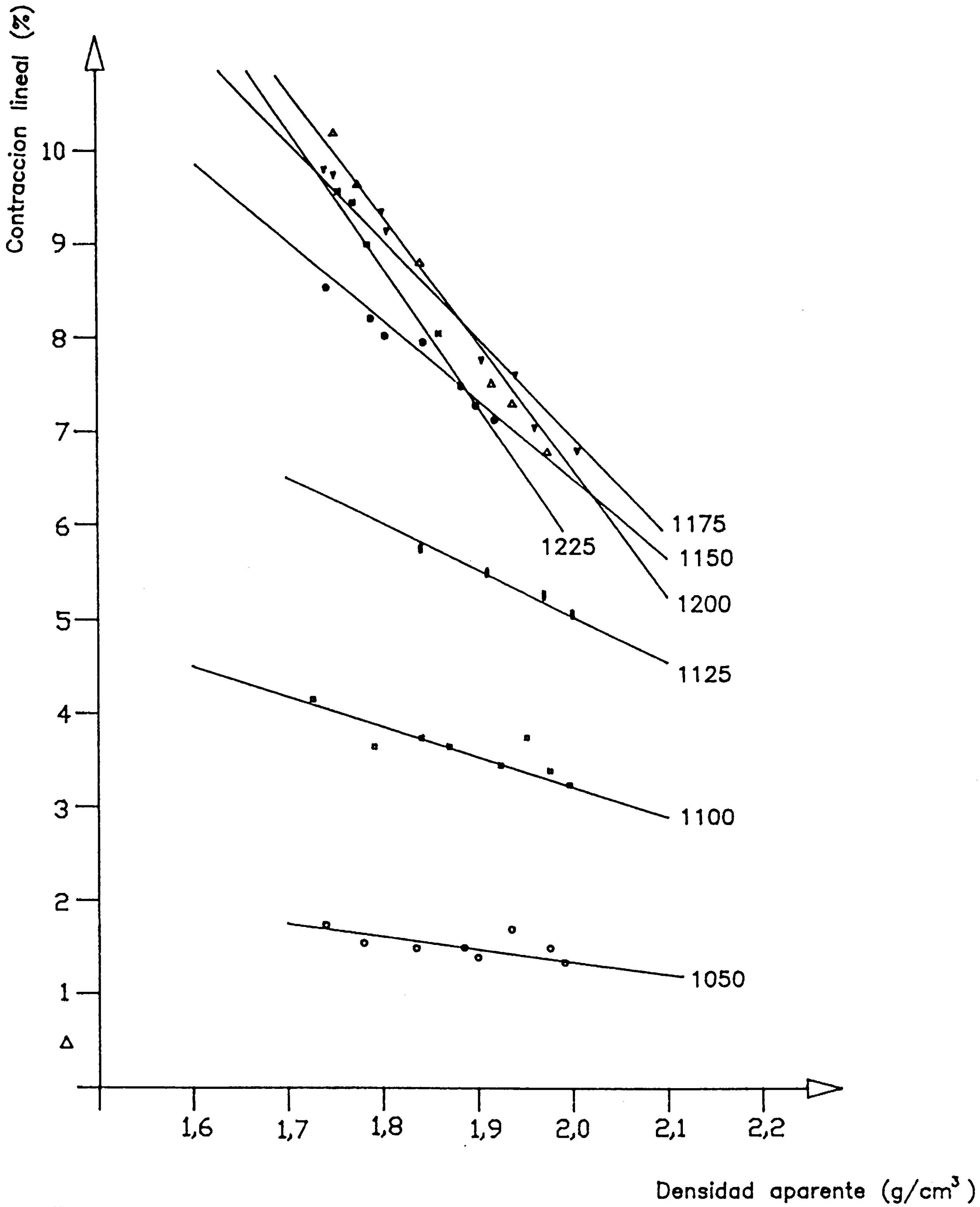


Figure 16

VARIATION OF LINEAL CONTRACTION WITH APPARENT DRY DENSITY AT DIFFERENT FIRING TEMPERATURES

Lineal Contraction (%)

Apparent density (g/cm3)

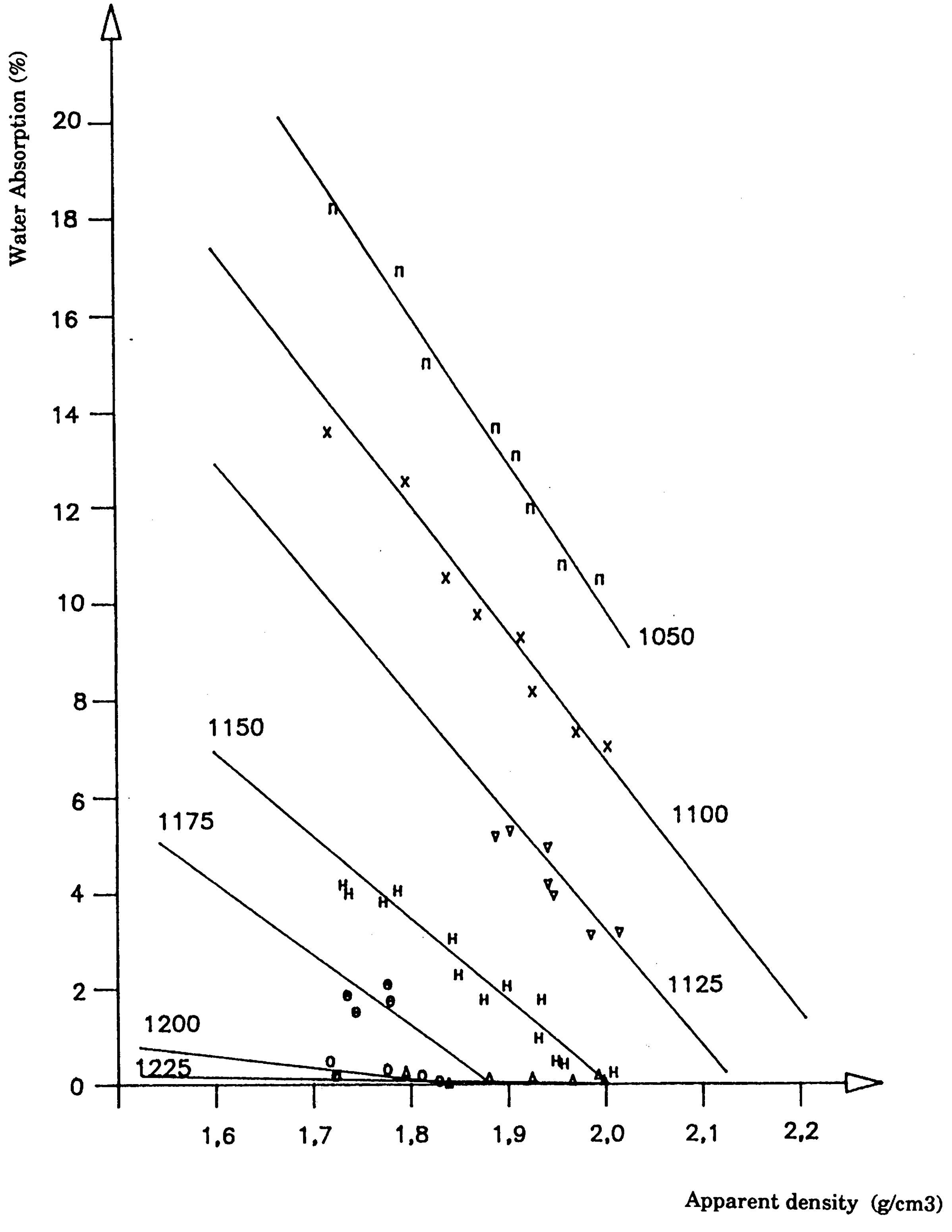
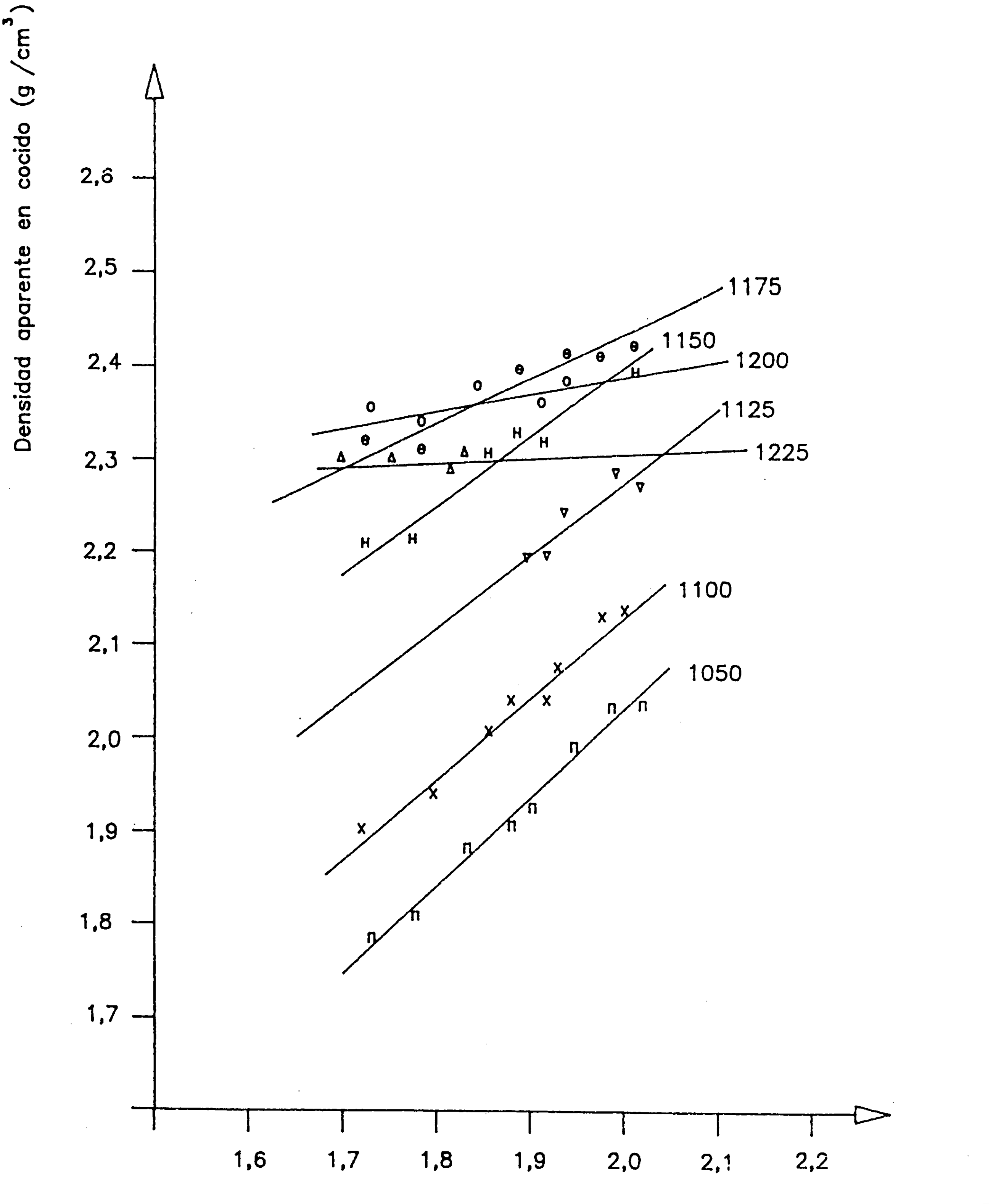


Figure 17.

VARIATION OF WATER ABSORPTION WITH APPARENT DRY DENSITY AT DIFFERENT FIRING TEMPERATURES



Apparent fired density (g/cm3)

Apparent dry density (g/cm3)

Figure 18

VARIATION OF APPARENT FIRED DENSITY WITH DENSITY AT DIFFERENT FIRING TEMPERATURES

a) As firing temperature increases, for a determined apparent dry density, the total porosity of the piece decreases (the lineal contraction and the apparent fired density increases), until a maximum density of the piece is reached.

b) Subsequent increases in temperature after the degree of maximum densification, notably reduce the density of the piece (total porosity is increased).

The development of apparent fired density and of lineal contraction with firing temperature corresponds to the behaviour, during the vitrification or sintering in the liquid phase, of compositions prepared from illitic-kaolinitic white clays and solvents rich in alkalines (basically K and Na). In fact, for these compositions and at higher temperatures than those at which the piece reaches maximum density, variations in lineal contraction and fired density with temperature are conditioned by two simultaneous and antagonistic effects that are developed in the piece as its apparent viscosity decreases. On one hand, the surface tension of the liquid phase present tends to reduce the size of the pores (open and closed) which increases lineal contraction and reduces the total porosity of the piece (open and closed). On the other hand, the expansion of gases occluded in the pores and/or generated by the decomposition of the haematite present (<1.0%), to form other more reduced species of iron oxide (Fe3O4, FeO, etc.) tends to increase closed porosity, consequently decreasing the lineal contraction of the piece. The result of these two opposing effects, that develop with the increase of firing temperature, causes the vitrification velocity to progressively decrease, up to a determined temperature Tcm. Above this temperature Tcm the pieces swells due to excessive expansion of the gases contained in its interior.

At firing temperatures much grater than Tcm, the viscosity of the vitreous phase can become sufficiently low to allow some of the occluded gases to escape, opening pores and thus increasing open porosity.

RELATIONSHIP BETWEEN PRESSING VARIABLES AND OPTIMUM DEGREE OF FIRING

Vitreous porcelain paving, falls within group BI, according to its classification by standard UNE 87, i.e. its absorption of water does not exceed 3%.

This classification is very broad and does not reflect the reality of this type of paving. Vitreous porcelain is an unglazed material, that can be polished and, in any case, has a minimum open porosity.

Figures 19 and 20 show two magnified photographs of industrially produced polished vitreous porcelain pieces, one of them with a water absorption value greater than 0.1%, in which the pores can be seen, and the other with a water absorption value less than 0.1%, which has much smaller sized pores.

As mentioned above, vitreous porcelain is normally polished, thus the presence of internal porosity (closed porosity), can give rise to pores on the surface of the piece when it is polished, as is seen in the photographs.

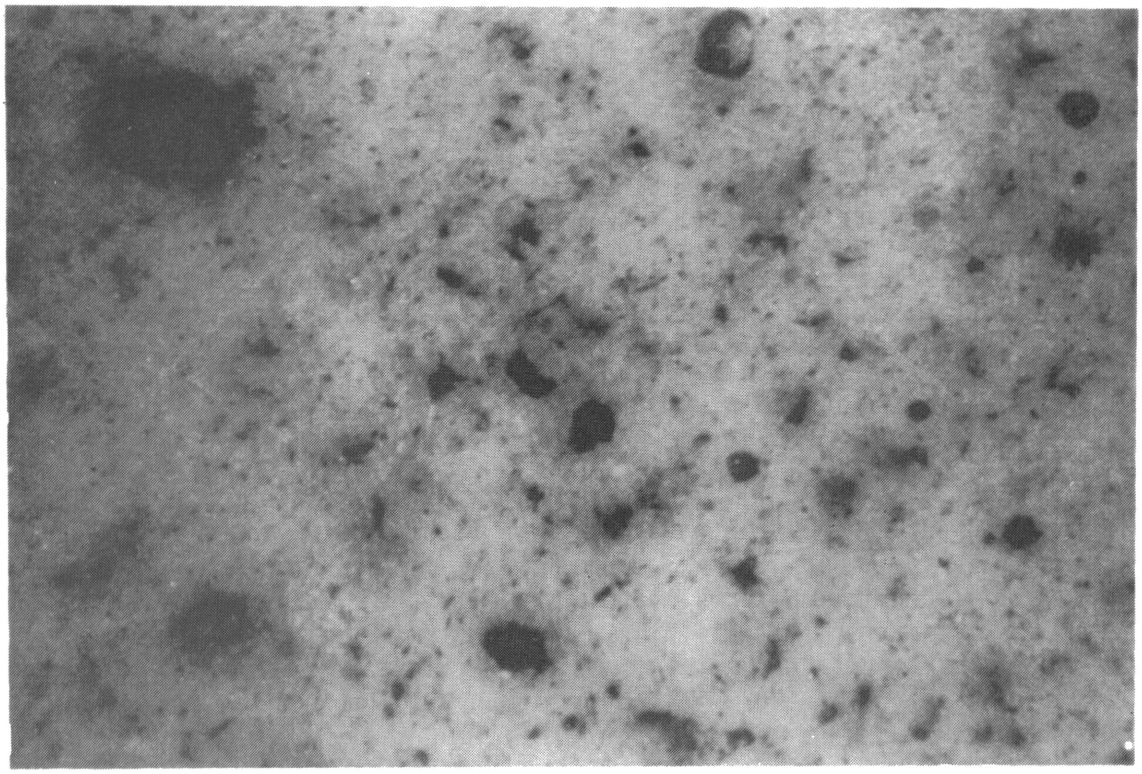


Figure 19. Magnified photograph of polished vitreous porcelain piece, W >0.1%

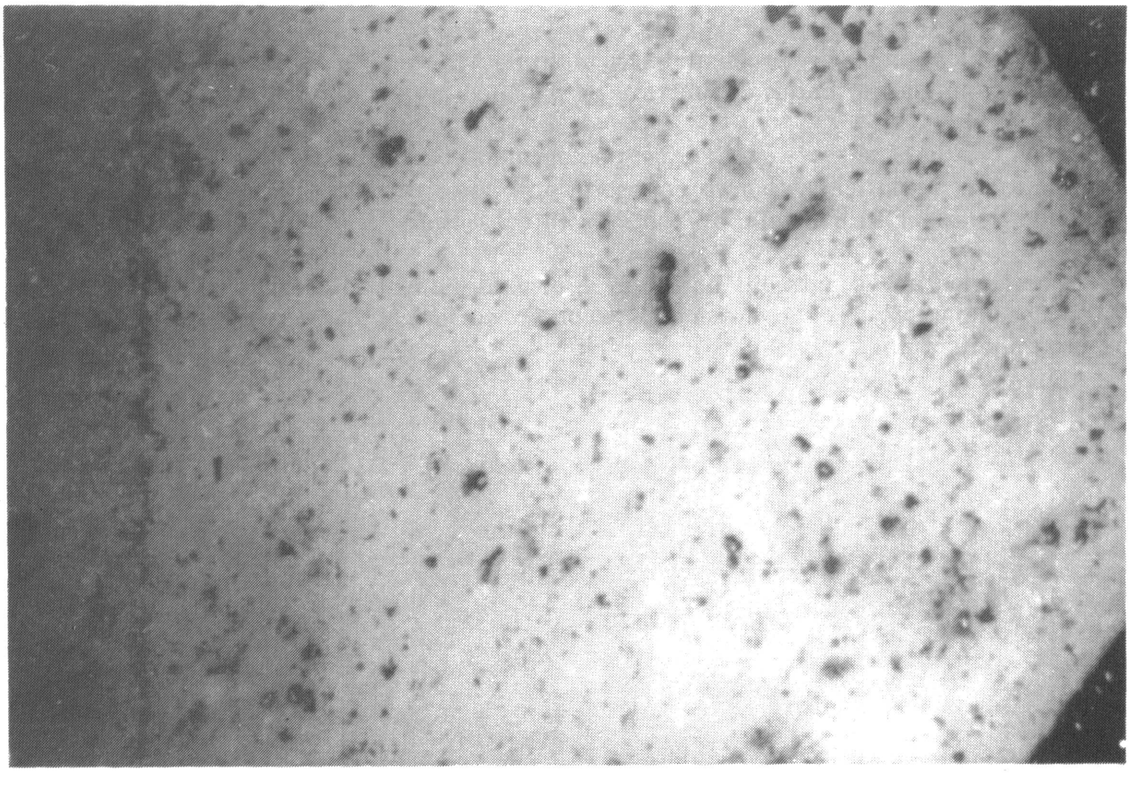


Figure 20. Magnified photograph of polished vitreous porcelain piece, W<0.1%.

RELATIONSHIP BETWEEN APPARENT DRY DENSITY AND OPTIMUM FIRING TEMPERATURE (Tcm)

As a consequence of all the above the optimum firing temperature (To) can be considered as that at which a piece of apparent density ρs must be fired (following the cycle used in this study) to reach a $W < 0.1\%$, the apparent fired density of the piece being at a maximum.

From figure 17 (graph of water absorbtion against apparent dry density, at different firing temperatures) the temperatures at which the water absorption was 0.1% were obtained for each one of the apparent dry densities, with which the tests were performed, by interpolation. (10)

The results obtained are shown in Table IX.

TABLE IX

Values of ρ_s and T for $W = 0.1\%$

ρs (g/cm³)	T (°C)
1.736	1225
1.782	1210
1.822	1195
1.840	1185
1.879	1170
1.914	1165
1.931	1160
1.976	1155
1.999	1150

A graph was constructed from these values (figure 21), in which the apparent dry density was plotted against the temperature for which water absorption is 0.1%.

As discussed previously, the optimum temperature is that at which, besides water absorption being a minimum, the porosity of the piece is at a maximum. In the case with which we are concerned, a value of $W = 0.1\%$ has been taken to obtain various optimum temperatures, the following step will verify that the fired pieces are not swollen at this temperature.

From the analysis of the results obtained it can be concluded that:

a) The optimum firing temperature decreases as apparent crude density increases.
b) For values of apparent density less or equal to 1.736, it is impossible to achieve an open porosity less than 0.1% without considerably reducing the apparent density of the piece (increasing its total porosity).
c) The increase of apparent dry density in the piece causes a decrease in total porosity of the fired piece.

Thus, to achieve a minimum closed porosity, without changing the open porosity, the piece must be moulded with a maximum apparent crude density.

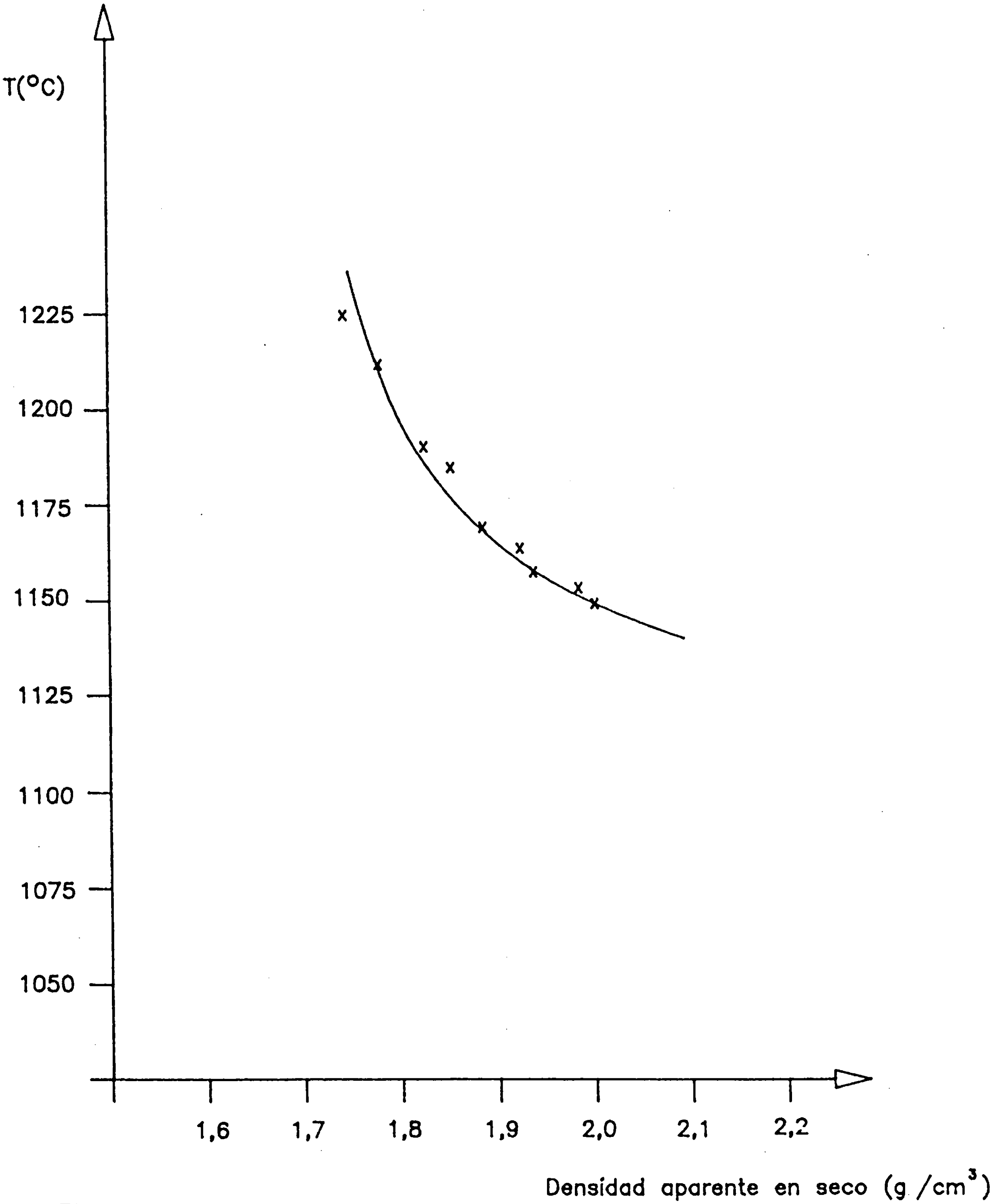


Figure 21

RELATIONSHIP BETWEEN FIRING TEMPERATURE AND COMPACTION NECESSARY TO OBTAIN WATER ABSORPTION LESS THAN OR EQUAL TO 0.1%
T (°C)
Apparent dry density (g/cm3)

MECHANICAL RESISTANCE AT OPTIMUM TEMPERATURE (W=0.1 %)

One of the technical characteristics that differentiates vitreous porcelain from other paving moulded by pressing is its high mechanical resistance when fired.

For the calculation of fired mechanical resistance, 6 sets of samples with different humidity contents were pressed at different pressing pressures.

The pressing pressure and humidity contents used were 200, 300, 400 and 600 kg/c2 and 2.5, 5.0 and 7.5% respectively.

After the samples were dried on a stove at 110oC, they were left to cool and then their apparent density was calculated (ρs).

With the apparent dry density (ρs) and according to figure 17, the optimum temperature at which the absorption of water will be 0.1% was obtained.

Each set of samples were fired a the corresponding temperature and after firing, they were submitted to a resistance to flexion test.

The mechanical resistance and the module of elasticity of the pieces were calculated from the test.

Table X shows the values of pressure and humidity used for moulding the pieces, as well as the apparent dry density (s), firing temperature (Tcm), calculated water absorption (W) and mechanical resistance (σc).

The values given here correspond to the arithmetic average of the 8 samples in each series:

TABLE X

P Kg/cm²	Xp Kg H_2O/kg ss	ρs g/cm³	Tcm °C	W %	σc Kg/cm³
300	0.025	1.840	1185	0.04	643
200	0.050	1.824	1195	0.04	634
300	0.050	1.879	1170	0.03	657
400	0.050	1.924	1160	0.05	668
600	0.050	1.976	1155	0.05	688
300	0.075	1.914	1165	0.02	663

From the results obtained, it can be concluded that mechanical resistance after firing is practically independent of the apparent dry density.

The samples have an open porosity, measured as water absorption capacity, less than 0.01% and thus, it may be said that the mechanical resistance of the fired piece only depends on the total porosity of the piece.

RELATIONSHIP BETWEEN INDEX OF PYROPLASTICITY AND APPARENT DRY DENSITY

To try to correlate the apparent dry density and the index of pyroplasticity (IP), 6 sets each containing eight 3 x 11 x 0.8 cm samples were pressed (11).

The pressures and humidity contents used, as well as the firing temperatures, were the same as for the previous section.

Table XI shows the average values obtained for each one of the sets.

TABLE XI

P Kg/cm^2	Xp Kg H_2O/kg ss	ρs g/cm^3	TcM °C	$IP.10^{-5}$ cm^{-1}
300	0.025	1.840	1185	4.1
200	0.050	1.824	1195	4.9
300	0.050	1.879	1170	3.5
400	0.050	1.924	1160	2.5
600	0.050	1.976	1155	1.8
300	0.075	1.914	1165	3.1

In figure 22 the variation of the pyroplastic index (IP) with apparent dry density is shown; it can be seen that, as the apparent dry density increases, the pyroplastic index increases.

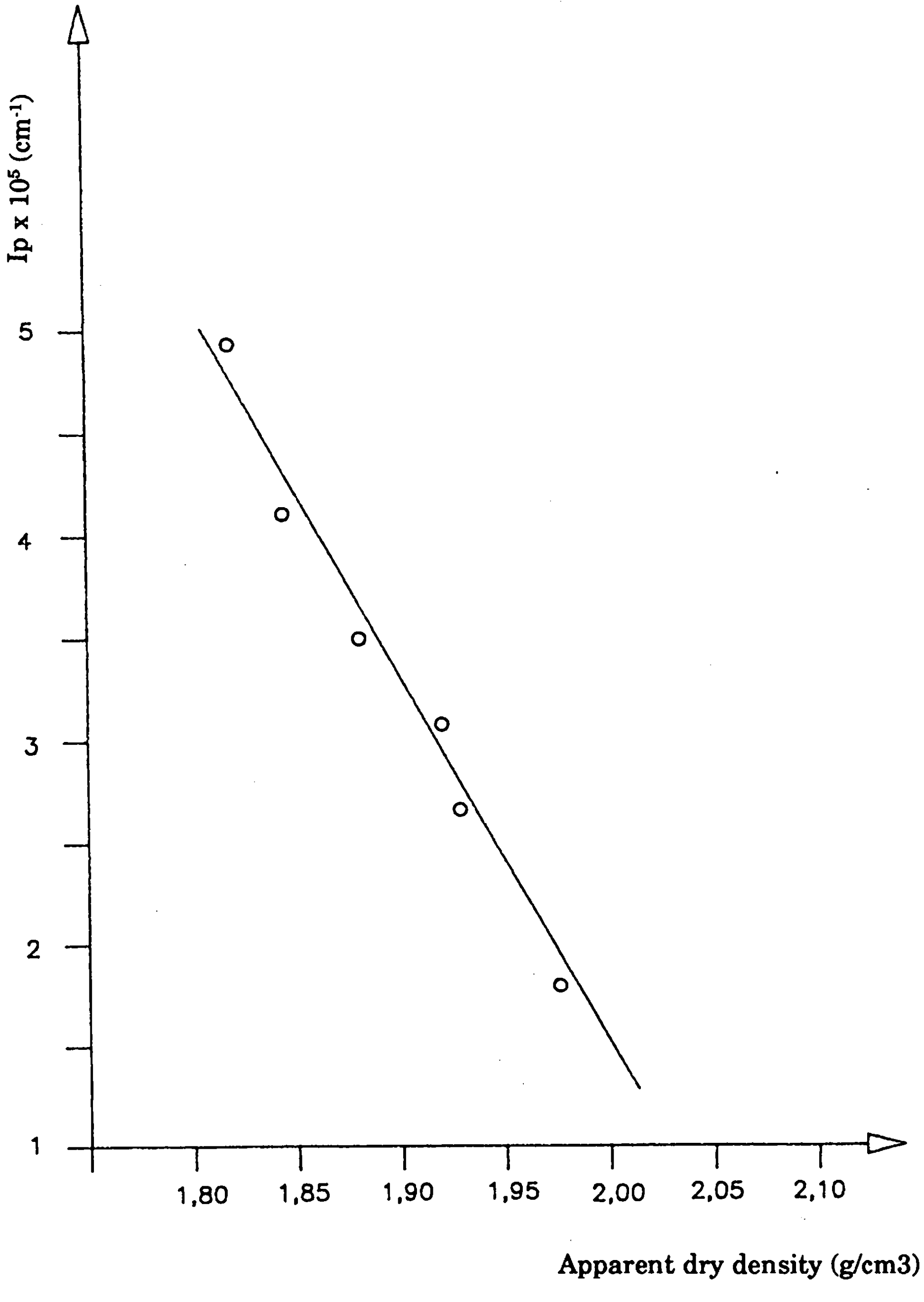


Figure 22.

Pyroplastic index against apparent dry density.

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