SUCTION OF LIQUIDS IN POROUS CERAMIC TILES

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1.- INTRODUCTION

1.1.- THE INTEREST OF LIQUIDS SUCTION IN THE MANUFACTURE OF CERAMIC TILES

The capacity for suction or absorption of water through the ceramic base is of great importance in the manufacturing of porous tiles. By absorbing water at its boiling temperature, the open porosity of the ceramic base is determined. Resistance to freezing is also intimately connected with the amount of water which the ceramic piece can absorb. Finally, the speed at which the ceramic base absorbs (or suctions) the slip water during the glazing operation is a determining factor of the time necessary for the layer of glaze applied to "dry" or become consolidated, with sufficient adherence for it to anchor onto the base well, and without the appearance of undulations or other textural problems which might affect the quality of the glaze resulting from the second firing.

1.2.- OBJECTIVE AND SCOPE OF THIS RESEARCH

This work is solely concerned with study of the speed of suction of liquids by fired ceramic tile bases, in order to find out the factors which influence that phenomenon. In this work an attempt will be made to obtain one or several correlations between those factors and the suction coefficient. This coefficient is intimately linked with the speed of suction of liquids by porous materials.

In order to achieve these objectives and to be able to apply the results on an industrial scale for the purpose of process control, it was felt to be indispensable to first design and construct a relatively simple but sufficiently accurate device for rapidly measuring the speed of liquids suction in porous ceramic pieces.

It was also necessary to propose a physical model (dynamic) based on theoretical considerations, to take in those properties of the liquid and those structural characteristics of the solid which might be related with the phenomenon of suction.

Finally, it was advisable to carry out trials with water at various temperatures, and with other liquids, using fired ceramic pieces of different structural characteristics, with a view to checking the validity of the proposed model.

In order to modify the structural characteristics of the fired pieces, the following courses of action were planned:

a) To take as bases powders of different characteristics and composition.

b) To add variable quantities of $CaCO3$ of given industrial composition.

c) To add different degreasing agents to that composition.

d) To modify the granulometry of the press powder.

e) To test different pressing pressure and humidity values.

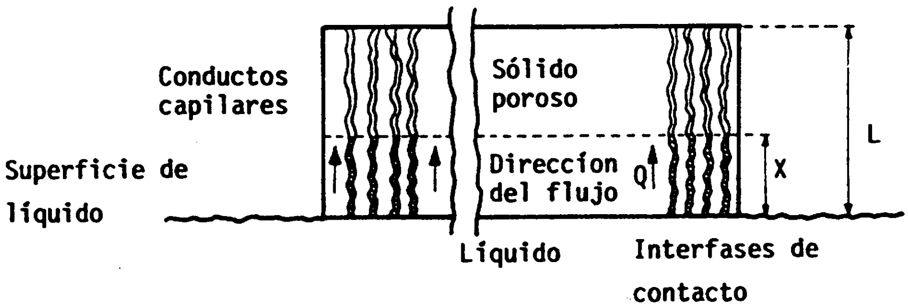
f) To use different firing cycles.

1.3.DYNAMIC MODEL PROPOSED

The porous structure of a solid cannot really be represented as a collection of numerous capillary conduits. For the purposes of circulation of a liquid through their pores, however, most porous solids can be taken to be composed of a complex mesh of capillary conduits taking a twisting path and having variable radius. This is the case of many ceramic products.

Given the difficulty of representing the complex texture of a porous solid in a physical model, recourse was had to the use of a greatly simplified model, similar to that proposed by KOZENY (8) for porous beds, consisting in assuming that the flow of a liquid through it is equivalent for all purposes to a hypothetical flow of the fluid throughout a maze of capillaries, of more or less twisting path, cylindrical, parallel and equal, laid out perpendicularly to the flat and parallel interfaces which bound the said solid (given the form of the test specimens used in this work and the usual form of the fired ceramic base upon which the glaze slip is applied).

This simplified model is shown in Figure 1.



1) Capillary conduits
2) Porous solid
3) Surface of liquid
4) Direction of flow
5) Liquid
6) Contact interphases

Fig. 1 - Simplified kinetic model

2.2.-APPARATUS

In order to carry out trials on suction of liquids through porous ceramic pieces, a piece of apparatus was designed according to the diagram shown in Figure 2.

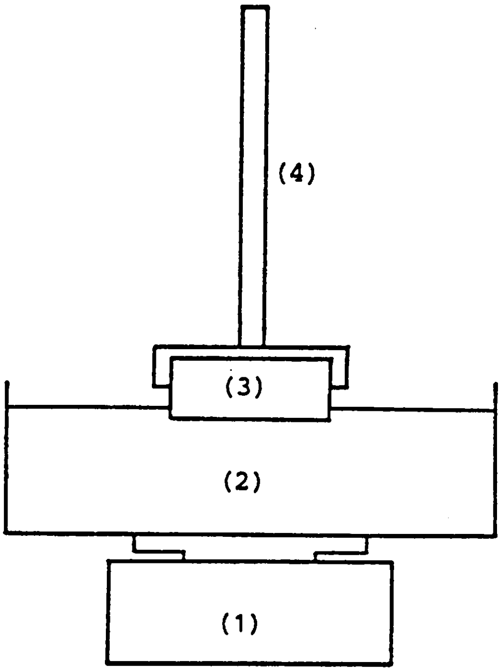


Figure 2. Assembly diagram.

For each fired test specimen used, the characteristics of its porous structure were determined (total porosity, dimensions, bulk density, permeability). The lateral surface of the test specimens was also rendered impermeable, so that the suction would always take place in an axial direction in each experiment.

By applying the equation of conservation of quantity of movement and the Law of Darcy to the model considered, and introducing the concept of average twistiness coefficient of the capillaries, the following equation was obtained, relating amount of water absorbed per surface area unit with the suction time (9):

$$\mu\sigma = [\frac{\sigma .\ r^2 - \varepsilon^2 - r_o - \cos \Theta}{2\mu - \lambda^2} t \ ] \ 1/2$$

This equation must in principle have the desired prerequisites. If a Ks (suction coefficient) magnitude is now defined, such that:

$$K_s = \rho \ (\sigma/\mu)^{1/2} \varepsilon \ / \ \lambda \ - r_o^{\ 1/2} \ [\cos \theta \ / \ 2 \ ]^{1/2}$$

and we obtain:

$$m_s = K_s - t^{1/2}$$

according to equation [2] the suction coefficient must depend upon a series of properties of the liquid (σ, μ, ρ, θ) and upon a series of characteristics of the porous solid (ε, r°, λ).

2.- MATERIALS, APPARATUS AND PROCEDURE

2.1.- MATERIALS

2.1.1.- Industrial body mixes

For carrying out of work under the various sections, the following five industrial compositions were used:

- A: composition used for the manufacture of buff body vitrified paving, prepared industrially by a process of humid process grinding in ball mill, with subsequent drying by atomization.

- B: composition used for the manufacture of buff body ceramic wall tiles by a process of traditional double firing. This is prepared industrially by dry process grinding in a hammer mill, subsequently adding the necessary humidity in a traditional dampening unit.

- C: composition also used for the manufacture of vitrified paving by a process of single firing in a roller kiln, with rapid firing cycles (45 min.). As for composition A, this is prepared by a procedure of humid process grinding.

- D: although used for manufacture of the same type of products as A, this is prepared industrially by dry process grinding in pendular mill, subsequently providing the necessary degree of humidity for pressing by means of a rotary granulater dampening unit.

- E: a composition used for the manufacturing of buff body porous wall tiles by a process of rapid double firing in roller kiln, with cycles of 45 and 35 minutes respectively for the first and second firings. The composition is prepared by humid process grinding in ball mill, with subsequent drying by atomization.

The five bodies used may be divided into two groups, according to their greater or lesser content of alkaline earth oxides, mainly present in them in the form of calcium carbonate.

a) Group with high carbonate content.

This group includes the compositions generally used for the manufacture of porous wall tiles, with calcium carbonate content of 14 to 16% (bodies B and E).

In these compositions the calcium carbonate content is introduced by means of natural clays - in this case Mas Vell clay. To this base clay are added others of low carbonate content to provide a resulting base with a series of properties such as plasticity, low expansion coefficient, lower porosity, etc., which facilitate the manufacturing process.

Industrial bodies B and E are made up of the natural clays mentioned below, mixed in the indicated proportions (percentages by weight):

	B	**E**
Mas Vell clay*	50 %	40 %
Chulilla clay*	25 %	40 %
Galve clay*	25	—
Moró clay*	—	20 %
	100 %	**100 %**

(*) All these clays are characterized in work previously published (10), (11), (12).

b) Group of low carbonate content.

This group includes the bodies described as A, C and D. These compositions have a carbonate content of less than 3% and are prepared with two natural red clays, Villar and Moró, mixed in differing proportions.

To composition C is also added 0.3% of manganese oxide, which acts as a fusing agent and oxidant, also lending the fired piece a darker colour.

The components of these three bodies are as follows (percentages by weight):

	A	**C**	**D**
Villar clay	70 %	60 %	70 %
Moró clay	30 %	40 %	30 %
	100 %	**100 %**	**100 %**

2.1.2.- ADDITIVES

Composition A, mentioned above, was modified by addition of different proportions of two additives, frequently used in industrial practice in order to increase its porosity and/or permeability.

i) CaCO3.

To supply calcium carbonate, a natural chalk of content higher than 99% by weight was used. This additive presented a very narrow granulometric distribution, with 75% (by weight) of particles having a size between 2 and 10 micras.

ii) Degreasing agents.

Separate use was made of the following degreasing agents:

- SE-6 quartz.
- SE-10 quartz.
- Sicron 100 quartz
- Kaolin waste.

The first three correspond to three degrees of grinding of a single quartz kaolinipherous sand, with content by weight in SiO2 of over 89%, the SE-6 quartz having the largest granulometry.

Kaolin waste is a low-cost by-product from obtaining kaolin from kaolinipherous sands. It is composed mainly of quartz and presents impurities of feldespar and kaolin; it contains 89% SiO2; its granulometry is similar to that of SE-6 quartz.

2.3.-OPERATIONAL METHOD USED IN THE SUCTION EXPERIMENTS

Once clamped in the stand, the test specimen was lowered until it touched the liquid (lowered some 3 mm below the surface of liquid). The suction time was measured from the moment the test specimen touched the surface of the liquid. The amount of liquid absorbed was measured for each time value, based on the loss of weight of the test specimen as recorded with the scales, also introducing a correction factor for the small variation of the push of the liquid on the test specimen throughout each experiment, owing to the almost imperceptible change in the level of the liquid due to suction. When working with volatile liquids, suitable correction was made for the evaporation which took place in the course of the experiment.

Each experiment was repeated three times in order to ensure repeatability, calculating the average of the three (almost identical) results obtained.

Between each two consecutive tests the liquid absorbed by the piece was eliminated by drying it at 110°C until it reached constant weight.

2.4.- DETERMINATION OF THE SUCTION COEFFICIENT

On representing the experimental results in the form ms (mass of liquid absorbed per m2 of solid transversal section) versus t1/2 (time elapsed since the beginning of the suction experiment), there should emerge a straight section of Ks slope, in accordance with the bibliography and with the kinetic model represented by equation [3]. This straight section must end when the liquid reaches the face of the cylindrical piece opposite the one which is contact with the liquid of the test specimen.

The representation obtained is like that shown in Figure 3, with a long straight section leaning with a positive slope, normally preceded by a short period of induction and followed by a final section which is not completely horizontal. According to LAUTRIDOU and OZOUF (13), this last section is due to the fact that the speed of displacement of the liquid through the capillaries is proportional to their radius, so that the liquid circulating through the capillaries of greater radius reaches the upper part of the piece quite some time before that which is circulating through the capillaries of smaller radius.

In accordance with this, the point of coordinates (m_s*,t*) of Figure 3, situated at the end of the straight section, would correspond to the end of the suction period, if only the capillaries of large size were taken into consideration (13). This m_s* will allow calculation of an effective suction porosity ε*, considering only the pores which take most part in the phenomenon of suction (9), by means of the expression:

$$\varepsilon^* = \frac{m_s^*}{\rho} \, \frac{1}{L} \qquad (4)$$

where L is the thickness of the piece or test specimen and δ the density of the liquid absorbed at operational temperature.

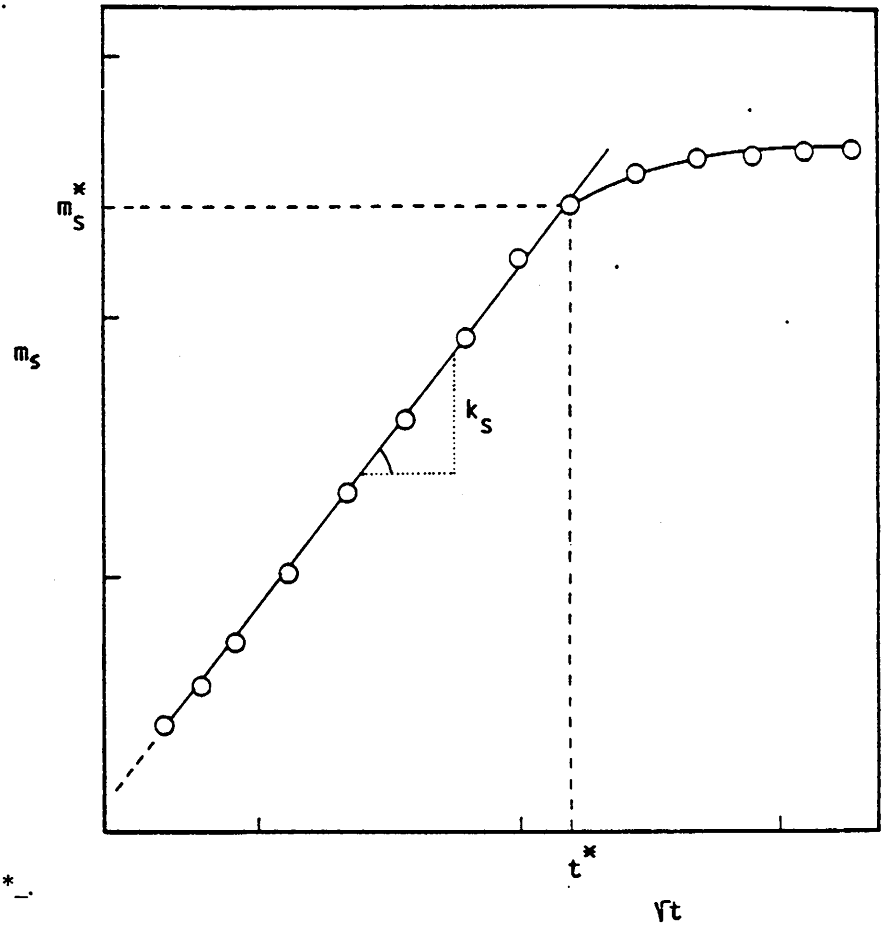


Figure 3.
Determination of Ks and m*_.

3.- RESULTS AND DISCUSSION

3.1.- INFLUENCE OF THE PROPERTIES OF THE LIQUID.

It is very important, for a given ceramic piece, to know the relationship which exists between the physical properties of the liquid which is absorbed and the suction coefficient. It is thus possible to predict or explain variations of the suction capacity observed in bases with respect to the slip water of the glaze applied, caused by variations in the temperature of the latter in the manufacturing of ceramic tiles by double firing. In order to take in a wider interval of variation of the physical properties of the liquid, seven experiments were carried out with water at different temperatures between 5 and 50°C (table I) and eight experiments with different liquids at 25°C (table II).

Experimentation with apolar liquids was undertaken with a view to possible utilization of one of them (preferably the 0- xilene) to determine indirectly the suction of water of pieces in the raw, as it is not possible to experiment directly with that liquid due to the total or partial destruction of the structure of the piece.

Identical test specimens having been used for all the experiments, the properties which depend on the structure of the solid remained constant. Grouping them together under a constant B, equation [2] can be written in the form:

$$Ks = \rho \, (\sigma / \mu)^{1/2} \, . \, B \, . \, (\cos \theta)^{1/2} \qquad [5]$$

or

$$\lg. (ks / \rho) = 0.5 \lg (\sigma / \mu) = \lg [B (\cos \theta)^{1/2}] \qquad [6]$$

By representing the experimental results of tables I and II in the form $\lg (K_s/\delta)$ versus $\lg (\sigma/\mu)$ (Figure 4), they conformed to a straight line of slope 0.509, in accordance with equation [6] of slope 0.5, which confirms the validity of equation [2] for relating suction capacity with the physical properties of the liquid absorbed in porous ceramic pieces.

From study of Table I it can be qualitatively deduced that, in a general way, increase of water temperature leads to increased suction coefficient. Consequently, in order to reduce slip water suction time of the fired ceramic base during the glazing operation one need only raise the temperature of the slip used, up to a certain limit.

TABLE I

Liquid: WATER

TEMPERATURE (°C)	K_s ($Kg/m^2 - s^{1/2}$)	ρ (Kg/m^3)	σ (N/m)	μ ($N\text{-}s/m^2$)
5	$13.32 - 10^{-2}$	999.99	7.49 - 10-2	$1.52 - 10^{-3}$
10	$14.24 - 10^{-2}$	999.73	7.43 - 10-2	$1.30 - 10^{-3}$
15	$15.73 - 10^{-2}$	999.13	7.35 - 10-2	$1.14 - 10^{-3}$
20	$16.21 - 10^{-2}$	998.00	7.27 - 10-2	$1.00 - 10^{-3}$
25	$17.40 - 10^{-2}$	997.07	7.20 - 10-2	$0.89 - 10^{-3}$
35	$19.79 - 10^{-2}$	994.06	7.04 - 10-2	$0.72 - 10^{-3}$
50	$22.91 - 10^{-2}$	988.07	6.79 - 10-2	$0.55 - 10^{-3}$

TABLE II

Temperature: 25°C

LIQUID	Ks (Kg/m2 - s1/2)	ρ (Kg/m3)	σ (N/m)	μ (N-s/m2)
Chloroform	25.25 - 10-2	1489.0	2.71 - 10-2	5.80 - 10-4
Acetone	14.73 - 10-2	792.0	2.37 - 10-2	3.26 - 10-4
n-Hexane	11.19 - 10-2	659.0	1.84 - 10-2	3.26 - 10-4
0-Xilene	10.07 - 10-2	881.0	3.01 - 10-2	8.10 - 10-4
Water	16.21 - 10-2	998.0	7.27 - 10-2	1.00 - 10-3
Glycerine-Water (50% p)	7.78 - 10-2	1126.3	7.00 - 10-2	6.05 - 10-3
Glycerine-Water (80% p)	3.07 - 10-2	1205.7	6.60 - 10-2	4.59 - 10-2
Glycerine-Water (85% p)	2.41 - 10-2	1219.0	6.60 - 10-2	8.15 - 10-2
Glycerine-Water (90% p)	1.86 - 10-2	1235.8	6.43 - 10-2	1.63 - 10-1

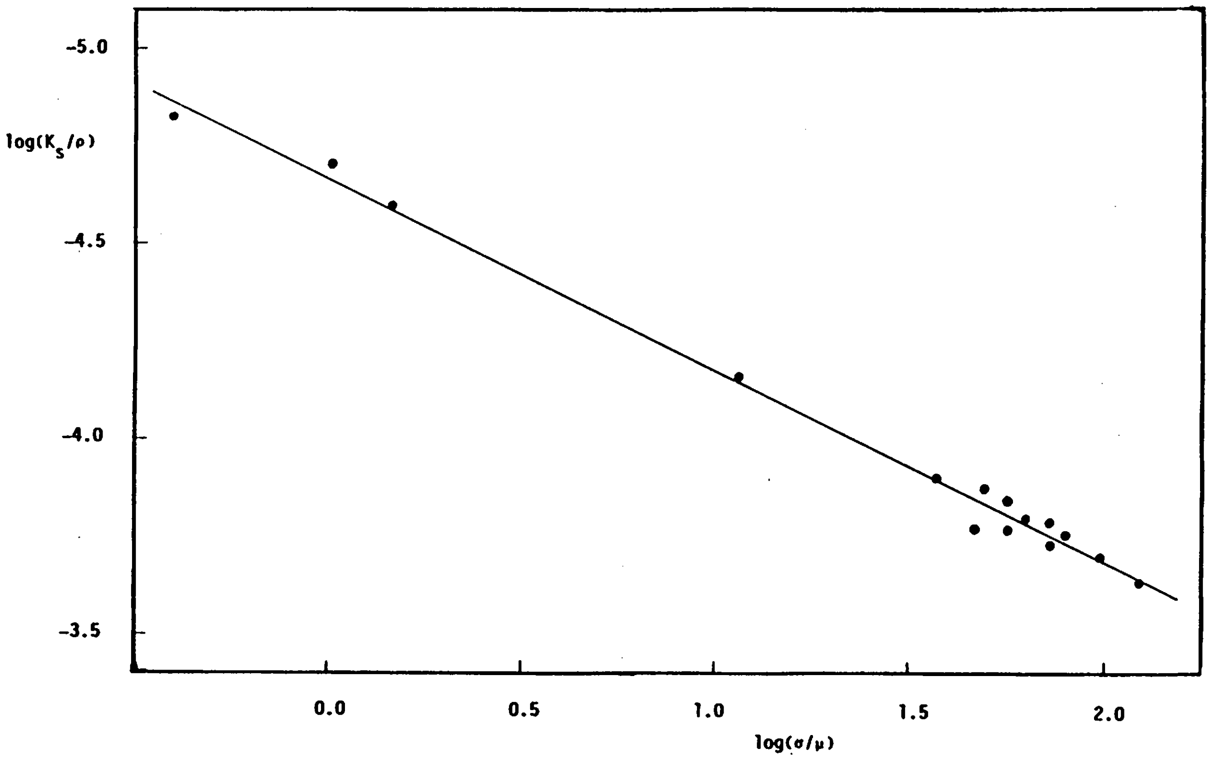


Figure 4. Variation of Ks with the physical properties of the liquid.

3.2.-INFLUENCE OF THE POROUS STRUCTURE OF THE PIECE

Various test specimens were prepared by using five different industrial bodies, modifying their calcium carbonate content, their degree of grinding, adding degreasing agents, testing different pressing conditions (pressing humidity and pressure), and by submitting the moulded pieces to different firing cycles, with the aim of finding out how these changes separately affected the suction coefficient of the fired piece.

3.2.1.- Influence of the composition and the characteristics of the press powder.

A study was made of the influence of various components (quality and quantity) which are included in the formulation of the material used to make the test specimens, and of the degree of grinding of the body, with a view to quantifying the way in which they affect the suction capacity of the fired pieces.

3.2.1.1.- Nature of the body.

Determination was made of various properties related with the porous structure of fired pieces for test specimens pressed under the same pressing conditions and fired with the same firing cycle, using industrial bodies A, B, C and D, and for test specimens made with industrial body E, for which, although it was pressed under slightly different conditions, the degree of compaction achieved in the raw was similar to that obtained with the other compositions.

The test specimens made with bodies B and E, which have a high percentage of calcium carbonate, were moulded without making any addition, while for those made with bodies A, C and D - with very low proportion of calcium carbonate - 2% of CaCO3 was added. Compositions A, B, C and D were pressed at a pressure of 300 kg/cm2 and a humidity of 0.065 (kg of water/kg of dry solid). Firing of the resulting test specimens was carried out for 30 minutes at a maximum temperature of 1050°C.

The test specimens made with composition E were pressed at a pressure of 250 kg/cm2 and a humidity of 0.070 (kg of water/kg of dry solid). Firing was carried out for 6 minutes at a maximum temperature of 1075°C.

Table III shows the values of the suction coefficient (Ks), permeability (Kp), effective suction porosity (ε*), pore radius corresponding to 16% of the total volume of the pores which correspond to those of largest diameter [ro(16)], and coefficient of twistiness (\) calculated with ro(16), obtained in the various determinations:

Sample	K_s ($^{Kg}/m^2 \cdot s^{1/2}$)	ε* —	$r_0(16)$ ———	$K_p \cdot 10^{15}$ (μm)	λ (m^2)
A-2	0.084	0.137	0.75	2.78	2.37
C-1	0.040	0.113	1.02	1.78	3.95
D-1	0.142	0.169	0.74	2.73	2.31
B-1	0.294	0.252	0.74	13.08	1.40
E-5	0.158	0.234	0.83	2.97	3.05

From study of the values obtained, the following may be concluded:

a) On comparison of the test specimen suction coefficients obtained with compositions B and E, with high carbonate content and therefore high effective porosities, it can be observed that the one made with composition B, of larger granulometry, has a greater suction coefficient in spite of the effective porosities of the two being very similar. This is probably due to the dry process grinding system leading to a much more open and more heterogeneous porous structure in the resulting fired piece. In fact, as may be observed, the permeability of test specimen B-1 is very much greater than that of the test specimens made with the other industrial body mixes.

b) On comparison of the test specimen suction coefficients obtained with compositions with low proportion of carbonates, it may be observed that the minimum value corresponds to composition C and the maximum to composition D. This may be due to the former having greater fusibility, so that the resulting fired piece has a lower effective porosity owing to the formation of glass phase. The second, on the other hand, obtained by dry process grinding, provides a higher effective porosity, possibly because its granulometric distribution is less suited to packing and the resulting pores in the fired piece are more accessible.

Overall, it may be appreciated that the test specimens made with the more fusible compositions have lower suction capacity, due to their open porosity being lower and the pores less accessible. The ones made with compositions prepared by dry process have more open porous structures and they have a higher suction coefficient.

For the purposes of process control, in order to achieve good suction coefficient it will therefore be advisable that the compositions used to make the pieces not be too fusible.

3.2.1.2.- Addition of $CaCO_3$.

A study was carried out of the influence of the addition of various proportions of CaCO3 to the formulation used, with a view to determining the effect on the properties of the resulting fired piece and its suction coefficient of variations in the content of that component.

Industrial body mix A was taken as a point of departure, and to it were added various proportions of CaCO3 ranging between 2 and 20 grams of CaCO3 for every 100 grams of original body mix, pressing and firing the test specimens under the same conditions.

TABLE IV

Sample	Y (*)	Ks ($Kg/m^2 - s^{1/2}$)	ε^* —	$r_0(16)$ (μm)	$Kpn \cdot 10^{15}$ (m^2)	λ —
A-1	—	0.090	0.148	0.63	2.66	1.93
A-2	2	0.084	0.137	0.75	2.78	2.34
A-3	4	0.111	0.167	0.85	4.13	2.32
A-4	6	0.138	0.180	0.91	5.20	2.33
A-5	8	0.149	0.190	0.85	6.43	2.00
A-6	12	0.176	0.203	0.83	7.69	1.85
A-7	16	0.186	0.211	0.83	8.89	1.76
A-8	20	0.203	0.213	0.89	11.60	1.69

(*) Y = kg of $CaCO_3$ added/100 kg of initial composition.

Table IV shows the results obtained. On analysis of these results it can be appreciated how in the interval of the compositions studied the value of the suction coefficient rises inevitably with the percentage of CaCO3, even to the point of doubling.

This increase of suction coefficient with the proportion of CaCO3 is mainly due to the increased porosity of the fired piece owing to progressive loss of CO2, to roasting of the carbonate and to the fact that the CaCO3 becomes increasingly refractory due to the formation of a calcic silicoaluminate network. All this leads to the formation of a more open porous structure with lower twistiness coefficients.

In industrial practice it will therefore be necessary for the carbonate content of the composition used for the manufacture of double firing porous tiles to be kept practically constant, so that the resulting biscuits (fired pieces) present uniform suction coefficients.

3.2.1.3.- Addition of degreasing agents.

The presence of inert degreasing agents, normally in the form of quartz, is quite common in industrial ceramic tile formulations, whose granulometry has to be selected in function of the effect desired.

In order to study the effect of degreasing agents present, several test specimens were prepared by adding to industrial body mix A the same percentage of degreasing agents of different granulometry. The test specimens shaped under the same pressing conditions were subjected to the same firing cycle. Table V shows the type of degreasing agent added and Table VI the granulometric distribution of each of them.

TABLE V

Sample	Y (*)	Quartz added
A-6	12	—
A-9	12	SE-6
A-10	12	SE-10
A-11	12	SICRON-100
A-12	12	WASTE No. 7

(*) Y = kg of $CaCO_3$ added/100 kg of initial composition.

TABLE VI

Differential granulometric analysis of the four degreasing agents used (% by weight of particles of each fraction)

Diameter (micras)	SE-6	SE-10	S-100	WASTE
Greater than 175	1	—	—	1
175 - 125	4	—	—	1
125 - 60	21	11	—	31
60 - 20	40	35	23	54
20 - 8	19	32	42	9
8 - 2	10	17	24	3
Lower than 2	5	5	11	1

The results obtained on the basis of the determinations carried out for the various series of test specimens are detailed in Table VII.

TABLE VII

Sample	K_s ($Kg/m^2 - S^{1/2}$)	ε^* —	$r_0(16)$ (μm)	$K\rho \cdot 10^{15}$ (m^2)	λ —
A-6	0.176	0.203	0.83	7.69	1.85
A-9	0.177	0.203	0.93	8.21	2.11
A-10	0.208	0.207	0.91	10.35	1.75
A-11	0.222	0.210	0.75	9.92	1.49
A-12	0.203	0.200	0.91	10.66	1.73

From study of these results, the following may be deduced:

The addition of degreasing agents produces an increase in the suction coefficient of the fired pieces, the increase being greater the finer the granulometry of the pieces.

When the degreasing agent is of coarse granulometry (SE-6), the mass porosity of the fired piece diminishes as a consequence of improvement of compaction in the raw, and although the size of the pores increases slightly the suction velocity hardly changes.

3.2.1.4.- Degree of grinding

In order to study the influence of the degree of grinding, three test specimens were prepared using industrial body mix B, which was submitted to an additional grinding of varying duration (30 and 120 min.).

Table VIII shows the additional grinding time used in each case. Similarly, with the most highly ground composition a test specimen was made up, shaping it under more drastic pressing conditions.

TABLE VIII

Sample	Additional grinding (time in minutes)
B-1	0
B-2	30
B-3	120
B-4	120 (*)

(*) Greater pressing pressure.

The results obtained are shown in Table IX.

TABLE IX

Sample	K_s ($Kg/m^2 - S^{1/2}$)	e^* —	$r_0(16)$ (μm)	$K_p \cdot 10^{15}$ (m^2)	λ —
B-1	0.294	0.252	0.74	13.08	1.40
B-2	0.368	0.278	0.67	13.61	1.31
B-3	0.412	0.306	0.60	11.10	1.23
B-4	0.258	0.259	0.53	6.04	1.41

From the results obtained it may be deduced that, for given pressing conditions, as the degree of grinding increases so too does the suction coefficient, possibly due to the increased porosity of the pieces obtained, with a granulometric distribution less suitable for packing of the particles despite the reduction in the average size of the pores.

Furthermore, on increasing pressing pressure, in order to obtain the same porosity in firing, the suction coefficient diminishes owing to the smaller size of the resulting pores.

Increasing the degree of grinding of the composition thus produces two opposing effects in the fired piece with respect to the circulation of fluid: an increase in its effective suction porosity (ε^*) and a reduction of pore size [ro(16)]. Both effects practically counterbalance each other with respect to the permeability (Kp) of the piece. The suction capacity of the fired piece, on the other hand, is more heavily influenced by the increase of its effective porosity.

3.2.2.- INFLUENCE OF PRESSING VARIABLES

In view of the fact that pressing pressure noticeably influenced the suction capacity of the resulting fired piece (samples B-3 and B-4) of Table IX), a study was made of the variables of piece moulding by pressing (humidity of the granulate and pressing pressure).

For this purpose a series of test specimens were prepared with industrial body mix E, under the varying pressing conditions detailed in Table X.

TABLE X

PRESSING CONDITIONS

Sample	PRESSURE (kg/cm2)	HUMIDITY (kg water/kg dry solid)
E-1	150	0.055
E-2	250	0.055
E-3	450	0.055
E-4	250	0.040
E-5	250	0.070

All test specimens were subjected to the same firing cycle, with 6 minutes at a maximum temperature of 1075°C.

3.2.2.1. Humidity of the granulate

TABLE XI

Sample	Pressing Humidity (kg water/kg d.s.)	$K\sigma$ ($Kg/m^2 \cdot S^{1/2}$)	e* —	$r_0(16)$ (μm)	$Kp\text{-}10^{15}$ (m^2)	λ —
E-4	0.040	0.308	0.259	1.00	10.86	2.04
E-2	0.055	0.229	0.236	0.85	6.00	2.26
E-5	0.070	0.158	0.234	0.83	2.97	3.05

On comparing these results, it may be observed that an increase of granulate humidity leads to lowered suction capacity due to reduction of the porosity of the fired pieces and the average size of their pores, owing to the lubricating effect of the water during pressing, which facilities drawing together of particles.

3.2.2.2.- Pressing Pressure

Table XII shows the results obtained with the series of test specimens made with a powder of the same humidity, subjecting them to different pressing pressures.

TABLE XII

Sample	Pressing pressure (kg/cm^2)	K_s ($Kg/m^2 \cdot S^{1/2}$)	ε* —	$r_0(16)$ (μm)	$K_p\text{-}10^{15}$ (m^2)	λ —
E-1	150	0.331	0.270	1.09	13.42	2.03
E-2	250	0.229	0.236	0.85	6.00	2.26
E-3	450	0.113	0.191	0.64	2.18	3.72

As may be observed, as pressing pressure increases the suction coefficient falls, for the reasons noted in the previous subsection, reducing to one third of its value on passing from a pressure of 150 kg/cm2 to a pressure of 450 kg/cm^2.

The results obtained in this section reveal the great importance of strict control of pressing conditions in order to ensure a suitable degree of suction in fired pieces, thus allowing maintenance of glaze application conditions within the desired limits. Variations of compaction between pieces or within a single piece will mean that they require different time to suction the glaze slip water following its application, which can create problems in the manufacturing process.

3.2.3.- INFLUENCE OF THE FIRING CYCLE

In order to study the influence of firing conditions on the suction capacity of the pieces, test specimens prepared with the same composition under identical pressing conditions were fired at different maximum firing temperatures, remaining for six minutes at those maximum temperatures and at a heating velocity of 60°C/min., up to 900°C (held for 25 minutes), and then on up to the maximum temperature used.

Composition E was used, shaping the test specimen under the normal pressing conditions of an industrial manufacturing process using atomized powder: 250 kg/cm2 pressure and a humidity of 0.055 kg water/kg of dry solid.

Table XIII shows the maximum firing temperatures used, and the values of the pressing variables.

TABLE XIII

Sample	Pressing pressure (kg/cm2)	Pressing humidity (kg water/kg d.s.)	Maximum firing temperature (°C)
E-2	250	0.055	1075
E-6	250	0.055	1025
E-7	250	0.055	1125

The results obtained are summarized in Table XIV.

TABLE XIV

Sample	Firing temp. (°C)	K_s ($Kg/m^2 \cdot S^{1/2}$)	ε^* —	$r_0(16)$ (μm)	$Kp \cdot 10^{15}$ (m^2)	λ —
E-6	1025	0.262	0.262	0.79	4.99	2.30
E-2	1075	0.229	0.236	0.85	6.00	2.26
E-7	1125	0.124	0.170	1.51	6.99	3.62

Composition E used contained a high proportion of alkaline earth oxides in the form of calcium carbonate, which could explain how in the temperature intervals considered there occurred a gradual reduction of porosity with increase in firing temperature, because the crystalline network, made up of calcic silicoaluminates which act as a skeleton or support which stabilizes the porosity of the pieces. Using a given firing temperature (1075°C in this case), this crystalline phase would begin to integrate into the glass phase, reducing porosity.

This behaviour is reflected in the value of the suction coefficient, which diminishes on increasing the maximum firing temperature of the pieces, especially above 1075°C. This reduction of suction coefficient occurs in spite of increased permeability and average pore radius of the piece, as a result of the reduction of porosity and, above all, due to the increase observed in the twistiness coefficient, probably due to the formation of a higher percentage of closed porosity.

In figures 5 and 6 the evolution of the porous microstructure of pieces fired under two different thermal cycles may be observed (test specimen E-2 and E-7) in microphotographs at enlargements of 2500 times. In these, the different state of sintering reached can be clearly observed, allowing the evolution of the texture of the piece with maximum firing temperature to be followed. As that maximum temperature increases the fine pores disappear and the coarse pores increase in size and become more rounded.

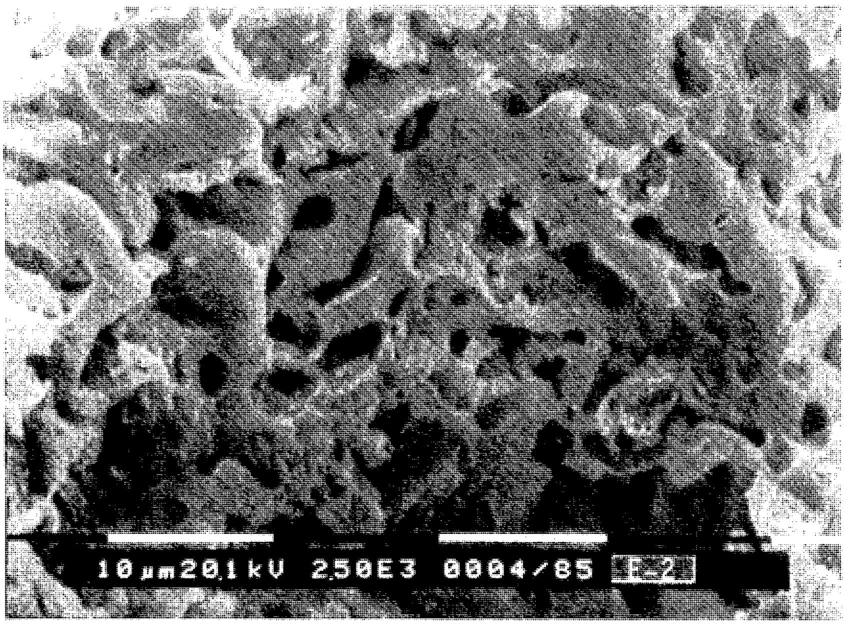


Figure 5. Microphotograph of test specimen E-2, enlarged 2500 times.

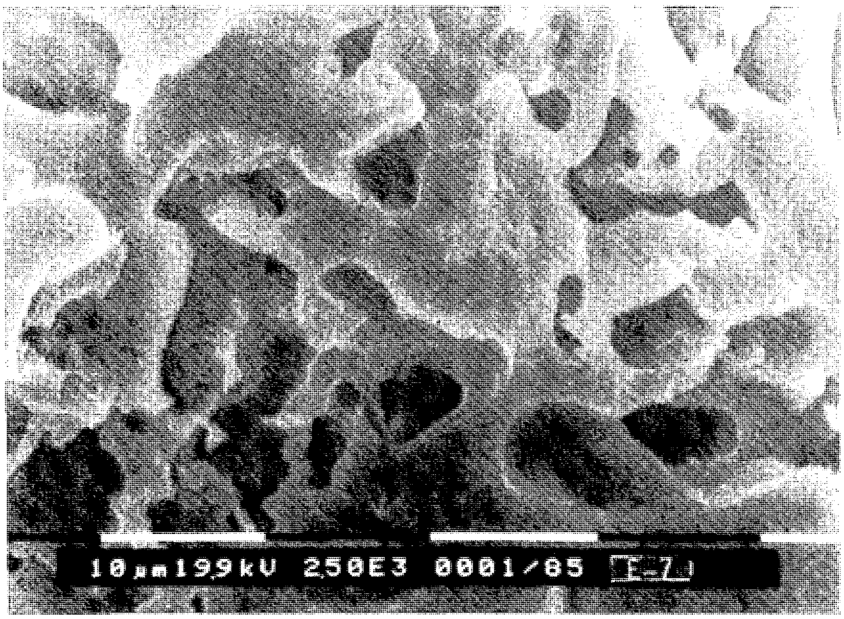


Figure 6. Microphotograph of test specimen E-7, enlarged 2500 times.

3.2.4.- ACCORDANCE WITH THE MODEL PROPOSED

For the experiments described in section 3.2 a single liquid was used - water at 25°C - and various steps were taken with the intention of modifying the porous structure of the fired piece and seeing how this affected its suction coefficient. In this subsection the aim is to check whether the properties of the porous structure of piece which appear in equation [2], listed in the form indicated in that mathematical expression, are suitable and sufficient to predict the changes in its suction coefficient which might arise as a consequence of the structural changes which derive from potential alterations of the composition, pressing conditions or firing cycle.

Since all the experiments described in section 3.2 were carried out with the same liquid (distilled water) and at the same temperature (25°C), the variables which depend upon the characteristics of the liquid (r_o, μ, p ò and θ) remained constant, so that by grouping them together in a constant C, equation [2] may be written as follows:

$$[7] \qquad Ks = C - (\varepsilon^*/\lambda) - r_0^{1/2}$$

Consequently, on representing the experimental results obtained for Ks compared to product (ε^*/λ)- $r_o^{1/2}$ in rectangular coordinates, a straight line should be obtained which passes through the origin of coordinates, as long as those results are in line with equation [2].

Figure 7 shows in this way all the results obtained in section 3.2. As may be observed, the experimental points are quite close to a straight line which passes through the origin. These results, together with those in section 3.1., confirm the validity of the dynamic model proposed and that of the equation [2] deduced in accordance with that model in order to relate the suction coefficient of fired ceramic pieces with the properties of the liquid absorbed and with the structural characteristics of the porous solid.

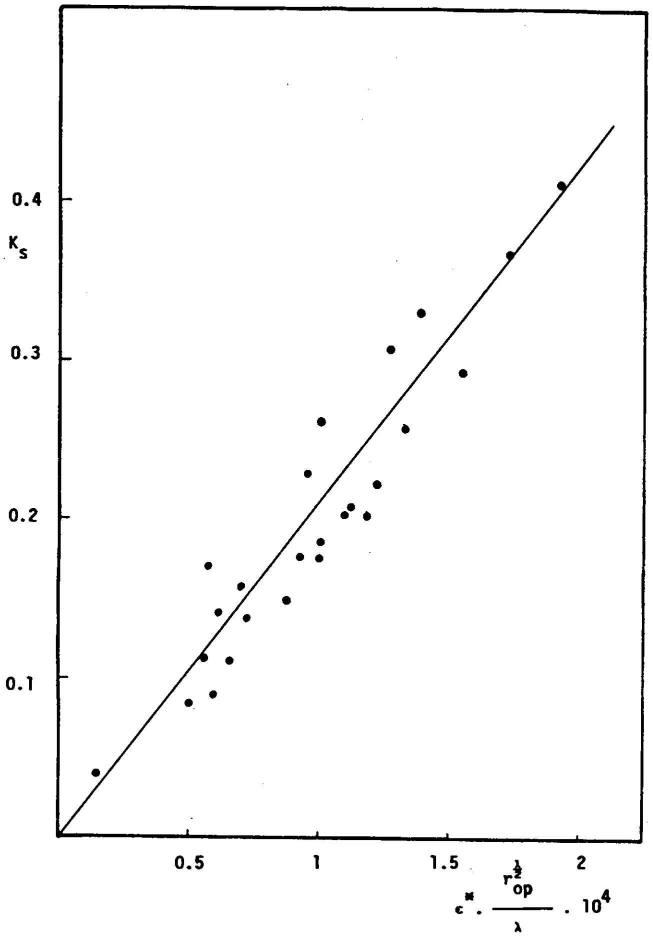


Figure 7. Adaptability of the results obtained to equation [7].

3.3..-SUMMARY OF RESULTS

Table XV summarizes the way in which the various major process variables qualitatively affect the suction coefficient, which is a conditioning factor in correctly carrying out the glazing operation in double firing, and the constant of gas permeability of the pieces, which is intimately connected with the degassings which arise and with oxidation of the "black core" during firing.

This table indicates the process variables which have to be controlled and the measures to be taken in an effort to maintain the properties of the piece within suitable limits with respect to permeability and suction capacity.

The constants of suction and permeability normally follow parallel paths, although permeability has a greater dependence on pore size.

TABLE XV (*)

	Pore Suction	Porosity size	Permeability	Suction velocity
Temperature of glaze slip	=	=	=	+
Dry process grinding	=	=	+	+
Addition of CaCO3	+	=	+	+
Addition of coarse inert matter	-	+	+	-
Addition of fine inert matter	+	+	+	+
Degrees of grinding	+	-	-	+
Pressing pressure	-	-	-	-
Granulate humidity	-	-	-	-
Firing	-	+	+	-

(*) + increases - decreases = does not affect

4.- CONCLUSIONS

From the work carried out and the results obtained, the conclusions summarized below may be drawn:

1. A piece of apparatus has been designed and constructed to improve a procedure which permits easy and rapid determination of the suction coefficient of porous ceramic pieces, using cylindrical test specimen of 50 mm diameter and 10 to 15 mm thickness.

2. A relatively simple equation has been deduced by analogy with the physical model proposed by KOZENY for circulation of fluids through porous beds, which relates the suction capacity of liquids in porous ceramic pieces with the properties of the liquid phase (viscosity, density and surface tension), the structural characteristics of the porous solid (average pore radius, porosity and twistiness coefficient) and the time used. This equation takes the form:

$$m_s = \rho\,(\sigma / \mu) - r_o^{1/2} - (\varepsilon / \lambda) - \cos\theta / 2\,)^{1/2} - t^{1/2} = K_s - t^{1/2}$$

3. In accordance with this equation of dynamic flow model, it was found that suction velocity is directly proportional to the density of the liquid and to the power 0.5 of its surface tension, while it is inversely proportional to the square root of its viscosity.

4. It was found that the model was complied with for liquids of different natures and at different temperatures, and for the various test specimens studied in which the porous structure of the piece was modified.

5. This model will permit prediction of variations of the suction capacity of pieces when the various process variables are altered, the repercussions of these variations on the porous structure of the pieces being known. With this information the manufacturing controls can be established which are necessary to maintain quality of the finished product with respect to the effect on it of correct implementation of the glazing operation in the manufacturing process of double firing ceramic tiles.

5.- BIBLIOGRAPHY

(1) Palmer, L.A., "Some absorption properties of clay bricks", B. S. Jour. Research, 3, 105 (1929).

(2) Gummerson, R.J.; Hall, C.; Hoff, W.D., "Water movement in porous building materials. II. Hydraulic suction and sorptivity of brick and other masonry materials", Building and Environment, 15, 101-108 (1980).

(3) Kirkham, D.; Feng, C.L., "Some tests of the diffusion theory and laws of capillary flow in soils", Soil Science, 67, 29-40 (1940).

(4) Vos, B.H.; Tammes, E., "Flow of water in the liquid phase", rep. No. BI-68-38/3P-11. Institute TNO for Building Materials and Building Structures." Rijswijk (Z.H.) (1968).

(5) Gummerson, R.J.; Hall, C.; Hoff, W.D., "Capillary water transport in masonry structures; building construction applications of Darcy's law", Construction papers, 1, 17- 27 (1980).

(6) Gummerson, R.J.; Hall, C.; Hoff, W.D., "The suction rate and the sorptivity of brick", Trans. J. Br. Ceram. Soc., 80, 150152 (1981).

(7) Hall, C., "Water movement in porous building materials. I. Unsatured flow theory and its applications", Building and Environment, 12, 117-125 (1977).

(8) Kozeny, J., "Uber Kapillare leiting des Wassers im Boden", Sitber. Akad. Wiss. Wien-Math-naturw. Klasse; 136 (Abt.IIa), 271-306 (1927).

(9) Beltrán, V.; Escardino, A.; Feliu, C.; Rodrigo, M.D., "Liquid Suction by porous ceramic materials", Brit, Ceram. Trans. J., 87, 64-69, (1988).

(10) Beltrán, V.; Bagán, V.; Sanchez, E.; Negre F., "Características técnicas de las arcillas utilizadas para la fabricación de pavimentos y revestimientos cerámicas en pasta roja", Técnica Cerámica, 164, 280-287 (1988).

(11) Bastida, J.; Beltrán, V., "Arcillas cerámicas de la provincia de Valencia", Bol. Soc. Esp. Cer. Vidr., 25 [4], 321-235 (1986).

(12) Escardino A.; Enrique, J.E.; Ramos, E., "Arcillas cerámicas de las Región Valenciana. II. Estudios de las arcillas de los yacimientos de las zonas de Sichar, Mas Vell, San Juan de Moró y Araya", Bol. Soc. Esp. Cer. Vidr., 17, [5], 285-291 (1978).

(13) Latidrou, J.P.; Ozouf, J.C., "Relations entre la gelivité et les propriétés (porosité, ascension capillaire) des roches calcaires". Colloque int. Unesco-Rilem. Alteration et protection des monuments en pierre. Paris, 5 June (1978).