THE EFFECTS OF THE APPLICATION OF SOLUBLE SALTS ON THE CURVATURE OF VITRIFIED FLOOR TILES

C.Doñate (*), J.Marco (*), E.Montiel (**), J.Martí (**)

(*) FRITTA, S.L.

(**) Institute for ceramic technology. University Jaume I, of Castellón.
Association for research of ceramic industries (AICE) Castellón (Spain).

SUMMARY

One of the characteristics of ceramic tiles with most influence on their later placing and use is their planarity, as the curvature of the pieces directly affects the facility of their placing and thus the finaly quality of the assembly of the coat. For this reason the control of the planarity is a basic item in the manufacturing process of ceramic tiles, in order to achieve the highest level of quality in the mentioned process.

An adequate control is based upon the knowledge of the variables of the product itself, as well as of the process, the influence of which can be important for the modification of the final curvature of the ceramic pieces.

In the industrial practice it has been found out that the addition of inorganic water-soluble salts affects the planarity of the pieces. This study tries to determine the mechanisms of how these salts affect the raw and baked piece, as well as the influence of several variables, all that in order to control the final curvature of ceramic tiles and thus to assure the adequate levels of quality.

1. FOREWORD

The obtaining of the quality levels that can be required of glazing ceramic tiles achieved through the process of single firing requires a knowledge and severe control of the variables of the product and the process.

The planarity of ceramic tiles is one of their main attributes.

The control of the property is at present carried out by means of modification of the piece's components (pate and enamel) and/or regulation of the firing cycle. In the manufacturing process it is not easy to achieve the dimensional stability required for ceramic tiles acting on these two variables.

The application of soluble salts on ceramic floor tiles, previous to the glazing stage, allows the disposal of a new regulating element for the planarity of the pieces.

In the present record, we study the influence of the application of a dissolved salt on some of the properties of raw as well as fired floor tiles, and an acting mechanism of the above mentioned salt is being proposed.

2. AIM AND EXTENT OF THE PRESENT STUDY

The addition of any dissolved salt on a piece provokes a modification of the composition of the treated area. The final effect on the product depends of the thickness of the piece that has been treated and on the type of the sált.

The aim of the present study is the determination of the acting mechanism of potassium carbonate applied on ceramic floor tiles.

The study has been divided into two phases:

- The effect produced by the addition of potassium carbonite in dissolultion on the composition and the curvature of raw pieces.

- The effect produced by the addition of potassium carbonate in dissolution on the properties of the fired product (absorption of water, linear shrinrage apparent density, curvature, thermical expansion).

3. USED MATERIALS AND EXPERIMENTAL PROCEDURE

3.1. MATERIALS

The salt used for the present study was potassium carbonate. Mixing different proportions of it with a spray-dried composition of the usually employed ones when obtaining vitrified floor tiles by single firing, the composotions indicated in table I have been prepared by humid milling, assuring this way a homogenious mixture of the spray-dried composition and the added salt.

Table I.- Tested Compositions

Reference	% Added K2CO3 (in weight)
1	0
2	1
3	4
4	8

Also industrially pressed pieces (45x45 cm2) have been used from the same spray-dried composition that has been used for the other essays.

3.2. EXPERIMENTAL PROCEDURES

In order to reproduce in the laboratory the effect produced by the application of soluble salts, the following scheme (figure 1) has been developped in experiments:

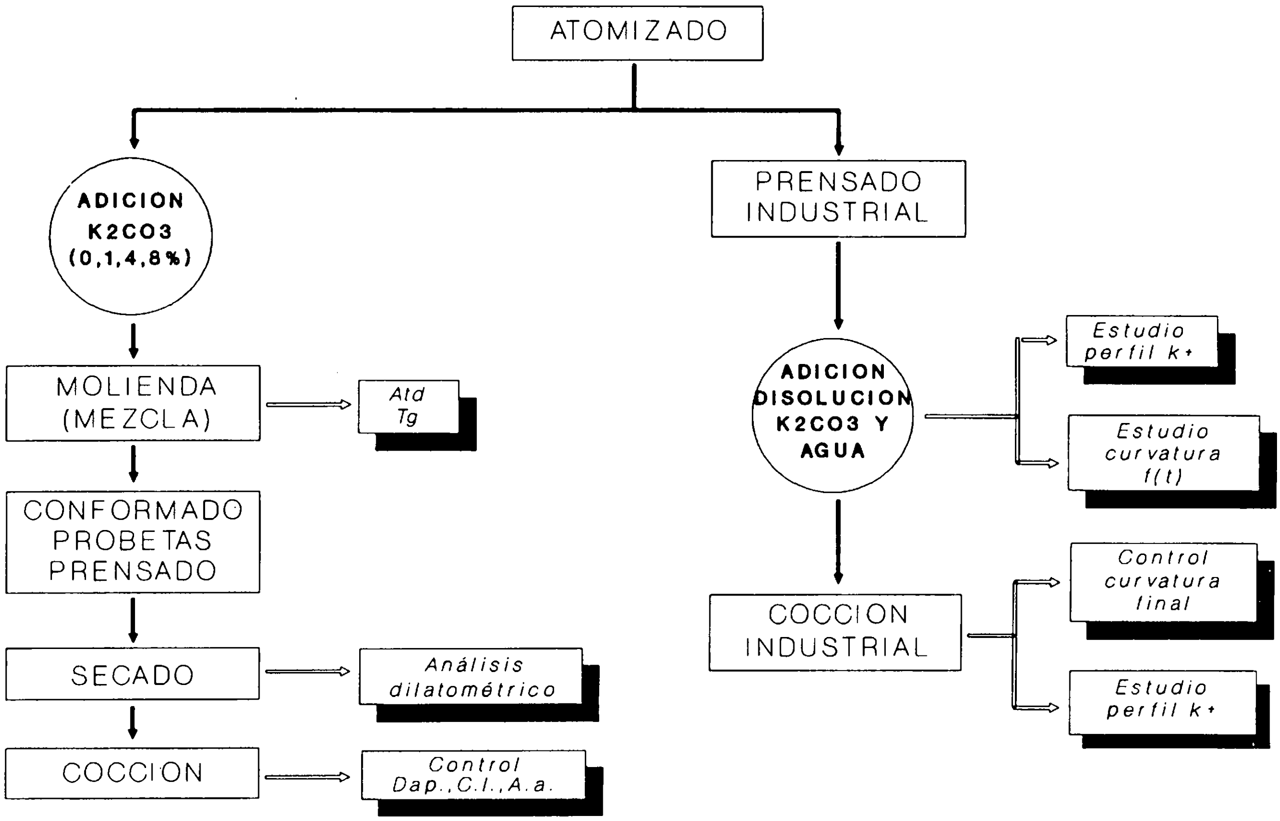


Figure 1. Experimental development scheme

3.2.1. EVOLUTION OF THE CENTRAL CURVATURE AND THE WEIGHT OF INDUSTRIAL PIECES, SOME TIME AFTER HAVING ADDED WATER AND/OR DISSOLVED SALT

By carrying out these assays we tried on the one hand to differentiate the effect due to the application of water and dissolved salts and, on the other hand to test if the last incorporation of water to the support, due to its glazing, affects the evolution of the curvature as well as the final curvature of the fired pieces.

To carry out this assay, the following experimental device has been used which will be shown in figure 2. After putting one piece on the support of the device and the other one in the scale situated next to it, the wanted quantity of water or dissolution has been applied and the data curvature-mass-time was measured. The initial temperature of the piece was about 70ºC in all the tests carried out.

The applications carried out were: 0'017 gr/cm2 of water; 0'026 gr/cm2 of dissolution 50:100 (potassium carbonate:water); 0'026 gr/cm2 of water; 0'026 gr/cm2 of dissolution 50:100 (potassium carbonate:water) and a later addition of 0'008 gr/cm2 of water.

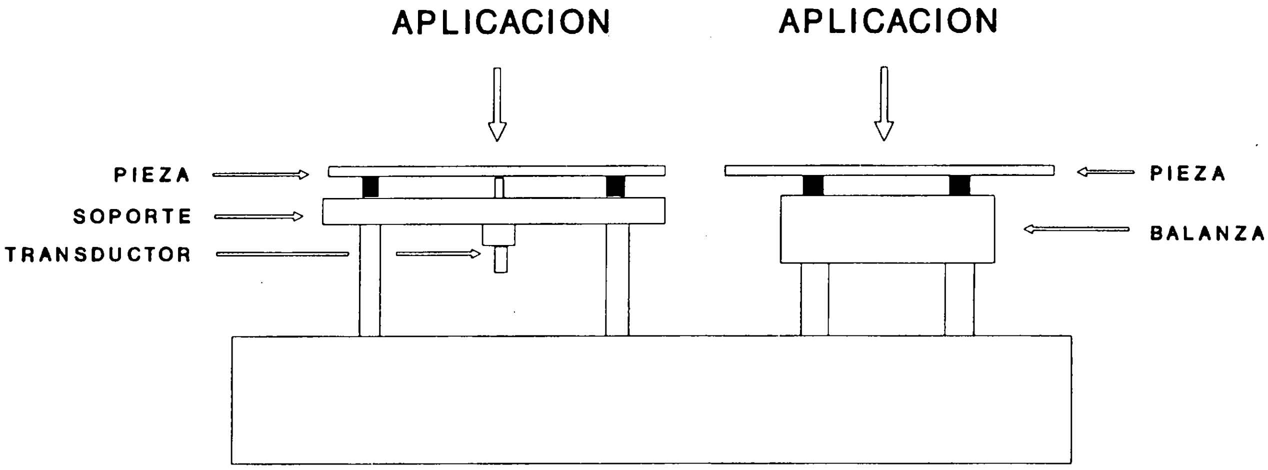


Figure 2.- Mounting scheme.

3.2.2. DIMENSIONAL DETERMINATION OF INDUSTRIAL PIECES

In order to achieve easily displayed data and to be able to quantify the effect produced by the application of the potassium carbonate solution, the curvature of the pieces has been determined by a measuring machine with the coordinates X-Y-Z, following the standard shown in figure 3. The measurement was carried out on the dry, piece, a piece with salt addition, and the fired piece.

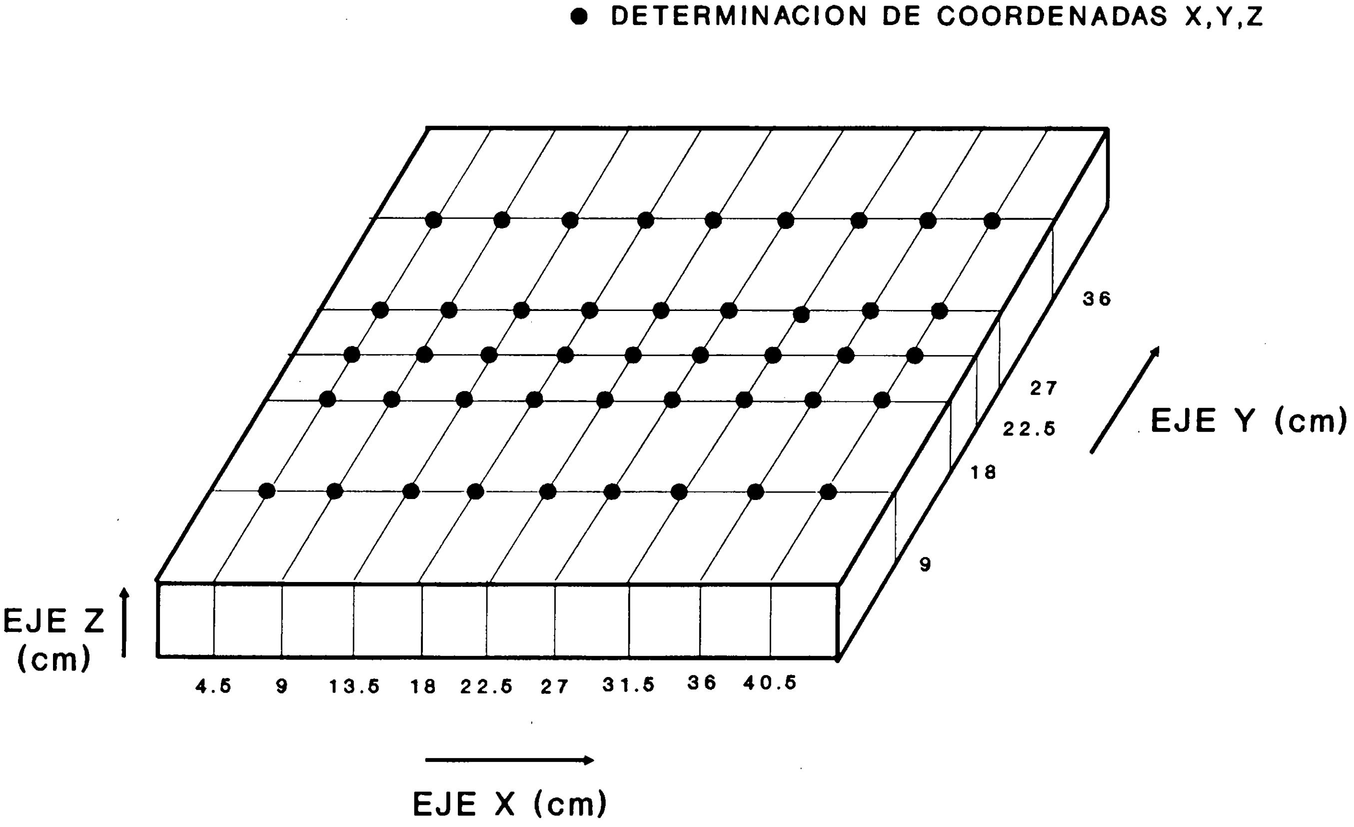


Figure 3.- Dimensional determination.

3.2.3. M.E.B. ANALYSIS OF THE PROFILE OF CONCENTRATION OF THE POTASSIUM CATION

A semi-quantitative microanalysis has been carried out by dispersive energies of x-rays (EDXA) of the pieces withsalt addition in a degassed electronic microscope (MEB).

The concentration values of the potassium ion from the surface to the inside of the piece have been measured.

3.2.4. DIAGRAMS OF LINEAR SHRINKCAGE - ABSORPTION OF THE WATER-TEMPERATURE OF THE PASTE ACCORDING TO THE DIFFERENT QUANTITIES OF ADDED SALT

With the compositions 1,2,3, 4 specimens with a diameter of 40 mm were filled with unidirectional pressing, after having fixed the value of the apparent density in dry in 1.90+/-0.01 gr/cc. The mentioned specimens were fired in an electrical lab kiln in a quick cycle to the maximum temperatures of 1090, 1110, 1130 and 1160ºC, staying 6 minutes at each of the tested maximum temperatures.

Water absorption, linear shrinkcage and apparent density of the specimens were measured.

3.2.5. DILATOMETRIC ANALYSIS

Samples have been prepared from the untreated specimens of the compositions 1 and 3, on which the dilatometric analysis in an absolute dilatometer with alumina support was carried out.

3.2.6. THERMO - DIFFERENTIAL AND THERMOGRAVIMETRICAL ANALYSIS

A thermo differential and thermogravimetrical analysis has been carried out of the compositions 1 and 3, with a heating speed of 10ºC/min.

4. RESULTS AND DISCUSSION

4.1. MODIFICATION OF PROPERTIES OF THE UNFIRED PRODUCT BY THE APPLICATION OF DISSOLVED SALT.

From figures 4 to 7 show the evolution of the curvature and of the mass depending on the time for the tested specimens.

In the figures 4 and 6 we can see an initial section in which the curvature becomes convex. This stretch coincides in the representation of mass-time, with an initial loss of mass. In a second section, the piece tends towards a concave curvature which coincides with a stabilization of the mass with the time.

This behaviour can be seen in pieces treated with water, leading to an interpretation, that at a first stage, a phenomenon of expansion takes place in the surface area of the piece by hydration of the clayed mineral leading to the curve as above indicated. At the same time a phenomenon of water diffusion towards inside can be observed, as well as a water absorption by the atmosphere on the lower side of the piece. This is the mechanism that finally makes the curvature be concave.

The general trend of the curves of pieces treated with the dissolution of potassium carbonate is similar to the before mentioned, although there are some differences to be seen, as a second convex curve after the evaluation towards the concave curvature has begun. This fact may be due to a rehydration of the added salt, thus producing an absorption of water on the upper side of the piece.

In effect, that mass-time curve seems to indicate this, as much weight is gained, coinciding with this phenomenon.

Both pieces, treated with salt only, as well as treated with salt and then with water show the behavoiur mentioned in the last paragraph, however, the later shows a less important phenomenon of rehydration. This fact may have two causes: the penetration effect of the salt in the support, when adding water, after the application of the solution K2Co3, difficulting the process of rehydration and/ or a decrease of this effect of rehydration of the salt by its application on the piece on the water side which is later absorbed.

Regarding the analysis of the central curvature of the piece in the sequence dry - sprayed, figure 8 shows the profiles for the different tested cases.

The same trend of the tested pieces can be seen, when they reach their final configuration (concave), when unfired tile, even though the speed at which the planarity of the piece is modified, is in every case different, as we have already observed.

The above mentioned speed must be in relation with the thickness of the piece treated with salt. Figure 9 shows the results of the measured concentration profiles of K+.

4.2. PROPERTY MODIFICATION OF THE FIRED PRODUCT

When seeing the before mentioned results, we could come to the conclusion that the application of K2Co3 on unfired pieces modifies the chemical composition of the upper part of the piece. The effect provoked by the introduction of a flux can affect some of the properties in a special way, as the thermal expansion and the speed of sintering of the affected area.

Table II shows the values of linear shrinkcage, apparent density in the firing and the water absorption, determined for the compositions, which are the object of the present study. A melting modification of the samples 2,3 and 4 can be seen, in comparison with 1 (without salt). Figures 10 and 11 show the variation of linear shrinkcage and the absorption of water depending on the percentage of the added K2Co3 at the different the addition tested temperatures.

In the mentioned figures we can see that the addition of 3% of the contents in K2Co3 to the spray - dry powder produce 1% variations of the linear shrinkcage, at approximate 1110ºC, with a minor influence on this variable when the firing test temperature increases.

The increase of melting of the tested compositions has to be mainly associated with the fusion of K2Co3 (897ºC) and the Possible modifications which this CAUSE in the synterisation of the clayed mineral.

TABLE II

VARIATION OF PHYSICAL PROPERTIES IN THE FIRING OF THE TESTED COMPOSITIONS

Reference	Apparent density in raw (gr/cc)	Temperature (Cº)	Apparent density (gr/cc)	Water absorption (%)	Linear contraction (%)
1	1.902	1090	2.139	8.88	5.24
	1.902	1110	2.194	7.51	5.90
	1.902	1130	2.330	4.17	7.59
	1.902	1160	2.428	1.06	8.70
2	1.893	1090	2.159	8.35	5.71
	1.893	1110	2.238	6.44	6.56
	1.893	1130	2.330	4.18	7.81
	1.893	1160	2.448	0.64	9.33
3	1.900	1090	2.217	5.90	6.65
	1.900	1110	2.285	4.74	7.50
	1.900	1130	2.370	2.68	8.53
	1.900	1160	2.380	0.00	8.67
4	1.891	1090	2.179	6.09	6.43
	1.891	1110	2.196	5.47	6.68
	1.891	1130	2.198	5.49	6.90
	1.891	1160	2.205	4.26	6.88

Figure 12 shows the results corresponding to the dilatometric analysis of unfired specimens of the compositions 1 and 3. The analysis of these results indicates an increase of the expansion and shrinkcage values, in the stages of heating and cooling, for the sample with addition of salt. The maximum values of expansion and contraction are shown in table III.

TABLE III

SAMPLE	MAXIMUM DILATATION	MAXIMUM CONTRACTION
1	9.46	67.11
3	11.27	72.82

Figures 13, 14 and 15 shows the curves ATD-TG-DTG of the used K2Co3 and of the samples 1 and 3.

Regarding the interpretation of the mentioned curves we can outline the fact that in the thermal analysis differential corresponding to the sample 3 the pick RELATED to the formation of calcium and/or magnesium phases does not appear, which can be observed in sample 1 at 967ºC. As well the picks corresponding to the loss of water of the hydroxides, dishydroxylation of the clayed mineral and a decomposition of the calcium and/or magnesium carbonates, in the spray-drying sample, at a higher temperature, at a higher altitude (thermal analysis differential) and with a bigger loss of weight (thermogravimetric analysis) than in the spray-drying sample with a 4% addition of salt.

These results clearly show the modification of the before mentioned chemical properties, which affects later the behaviour of the material during the firing stage.

This modification, as we have already mentioned before,comes from the different composition of the upper side of the piece; Figure 16 shows the profiles of concentration corresponding to the pieces treated with 0'026 gr/cm2 of dissolution K2Co3 : water (50:100) and 0'026 gr/cm2 in the mentioned dissolution plus 0'08 gr/cm2 of water, industrially fired.

The modifications of the composition by addition of potassium carbonate produces, as we have been able to confirm, an alteration of the materials' behaviour during the firing. Thus, the final planarity of the pieces is affected, as can be seen in figure 17, 18 and 19, for pieces treated with water, K2Co3 dissolution and K2Co3 dissolution + water. These figures are obtained by means of a simulation on the computer using the data obtained by the determination of the coordinates X-Y-Z.

In the mentioned profiles we can see that the pieces treated with salt maintain a concave final curvature, while those treated with the usual procedure, with the same contribution of water and enamel, show a convex curvature.

These results can be seen when superposing the dry and firing profiles in the central zone of the piece, at a value of Y=22.5 cm, as figures 20 and 21 show.

The explaination of this results is related to the modification, as mentioned before, of the chemical composition of the surface layers of the support which has been treated with the K2Co3 dissolution (until the limit of penetration). This phenomenon, according to the fluxing results and the coefficient of dilatation results in contraction differences in the supports' hollow, as to be seen in figure 22, affect the final curvature of the fired pieces.

On the other hand, in pieces of industrial production, one has to consider, besides the effect of the support, the effect of the enamel coat. Following the scheme shown in figure 23, one can verify how the final effect on enamel and support, results in a minor curvature in pieces treated with K2Co3 dissolutions before the enamelling process.

5. CONCLUSIONS

We get the following conclusions from the present study:

1. The application of soluble salts in a water dissolution on green tiles pieces of floor, in the stage before glazing provokes variations of the evolution of the curvature of undfired pieces. However, the final curvature of the raw pieces is similar to the ones treated with an equivalent quantity of water to the quantity brought to the piece during the glazing process.

2. The surface application of a potassium carbonate dissolution produces modifications in the piece's behaviour. It has been verified that from the different percentages of added potassium carbonate, the addition corresponding to 4% provokes most modifications in the tested variables. Concretely, the type of body fired at a temperature of 1100ºC has an 1.6% as shrinkcage more than when treated with K2Co3. This fact has been verified by the determination carried out in the dilatometric analysis.

3. The acting mechanism of potassium carbonate dissolutions applied on supports of vitrified floor tiles at a previous stage to the glazing process, is based upon the diffusion of the salt towards the inside of the support by means of the effect of the added water in the different applications of the enamel. The support layer that presents potassium carbonate (until the limit of the salt penetration), shows a different chemical composition than the rest of the support. This way we obtain a more fluxing coat in its upper part, which shows an increase of contraction during firing. This effect, in combination with the enamel effect, allows us a new possibility of regulation of the planarity of the pieces.

4. By means of the application of soluble salts, the final curvature of vitrified floor tile ceramic pieces can be regulated, when adapted to the product to be proceded. One has to take into account that the procedure is very delicate and modifications of the quantities of added salt provoke important variations of the properties.

6. BIBLIOGRAPHY

(1) Kirk-Othmar. Encyclopedia of Chemical Technology.
John Wiley & Sons. New York. Third Edition, 1981.

(2) J.M. Fernández Navarro
"The glass. Constitution, fabrication and properties" Ed. CSIC, 1985.

(3) J.E. Enrique, F. Negre, A. Blasco, V. Beltrán
" Controls of the manufacturing of floor tiles and ceramic cloaks". Association of Research and Ceramic Industries., 1990

(4) J.L. Amorós, A. Moreno, F. Negre, M.J. Orts
"Agreement enamel-support (IV). Nature of the interphase enamel-support". Ceramic technique, nº 181 (130-145), 1990.

(5) J.E. Enrique, F. Negre
" Ceramic technology Volume V. Ceramic enamels". Institute for technical chemistry.
(ceramic technology) University of Valencia, 1985.

(6) J.E. Enrique, A. Blasco, M. Monzó, J.L. Amorós
"Ceramic tables". Institute for technical chemistry (ceramic technology) University of Valencia, 1984

(7) Robert. C. MacKenzie
"The Differential Thermal Investigation of Clays" Mineralogical Sovety
(Clay mineral group). 1957.

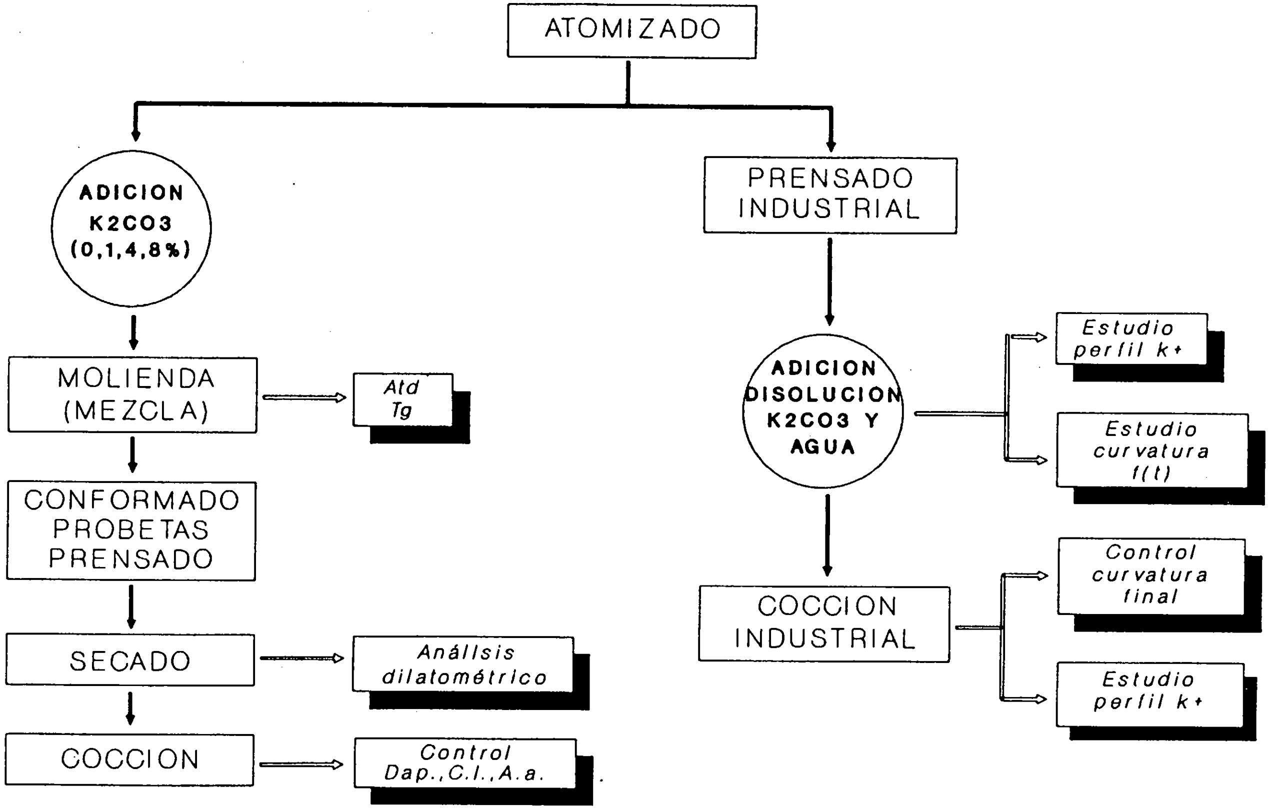


Figure 1.- EXPERIMENTAL DEVELOPMENT SCHEME

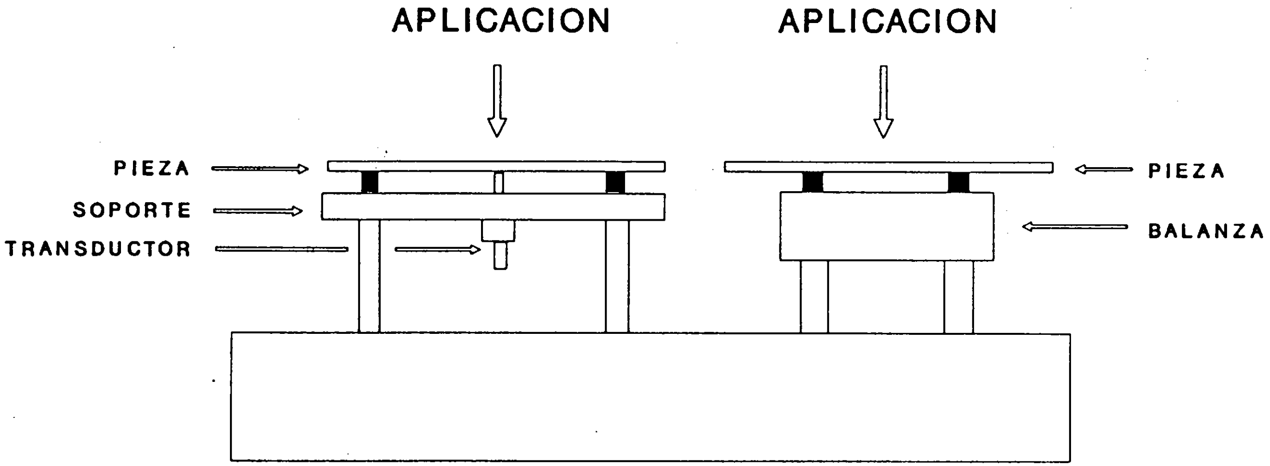


Figure 2.- MOUNTING SCHEME

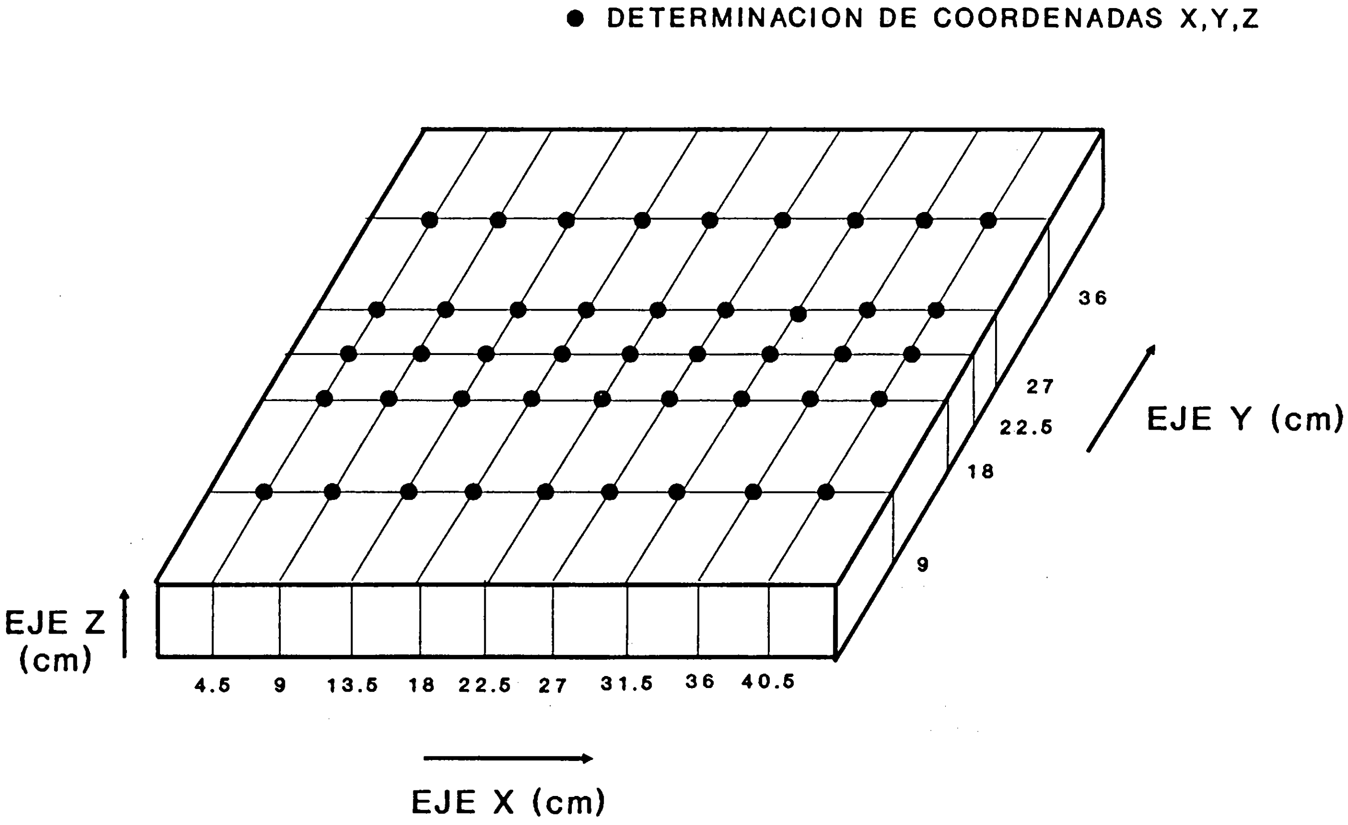


Figure 3.- DIMENSIONAL DETERMINATION

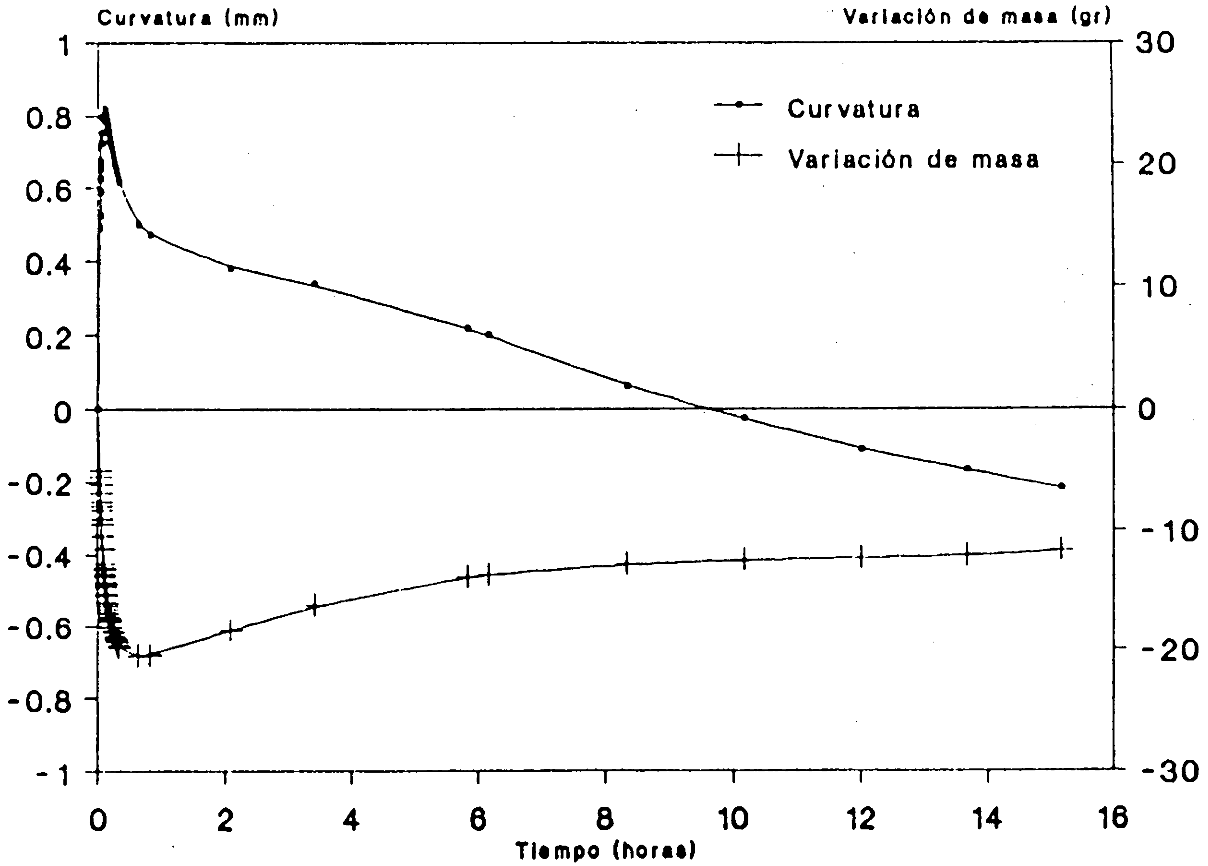


Figure 4.- VARIATION CURVATURE/MASS WITH THE TIME
APPLICATION OF 0'017 gr/cm2 OF WATER

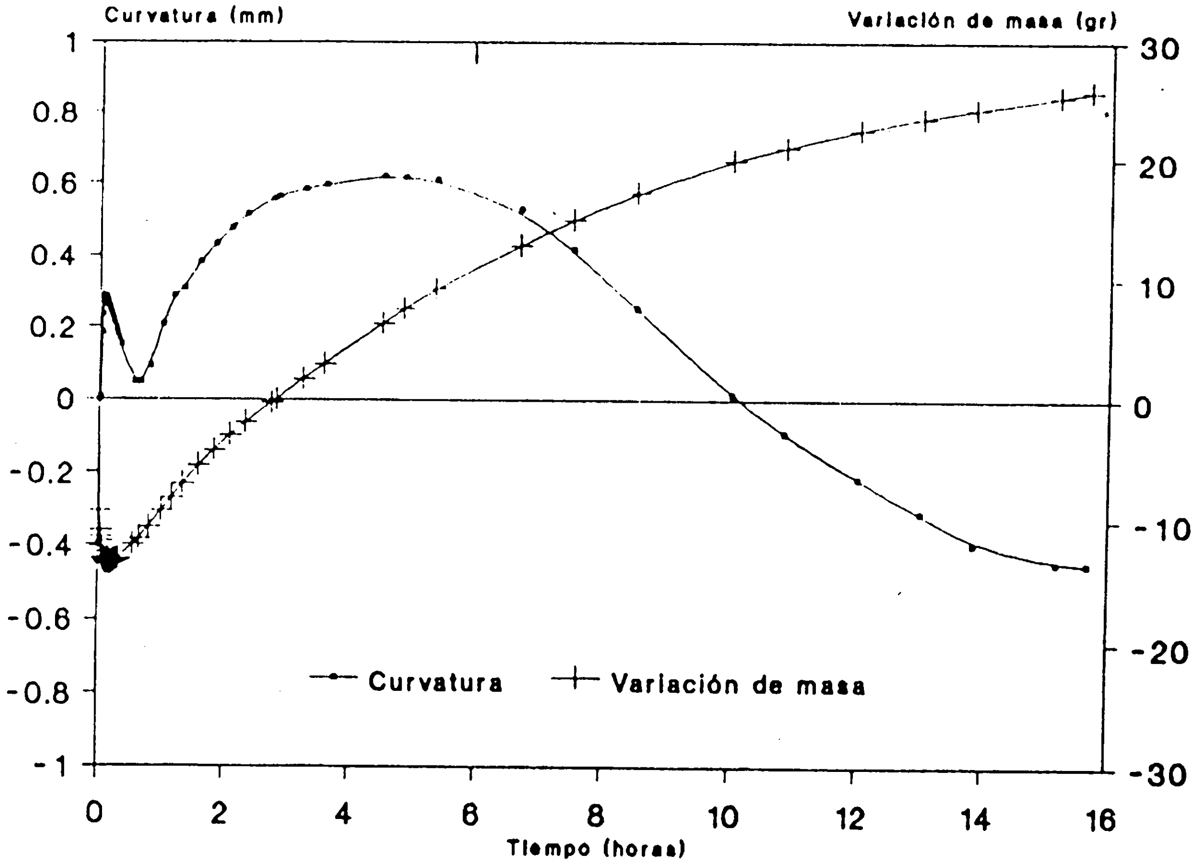


Figure 5.- VARIATION CURVATURE/MASS WITH THE TIME APPLICATION 0'026 gr/cm2 of K2Co3 50:100

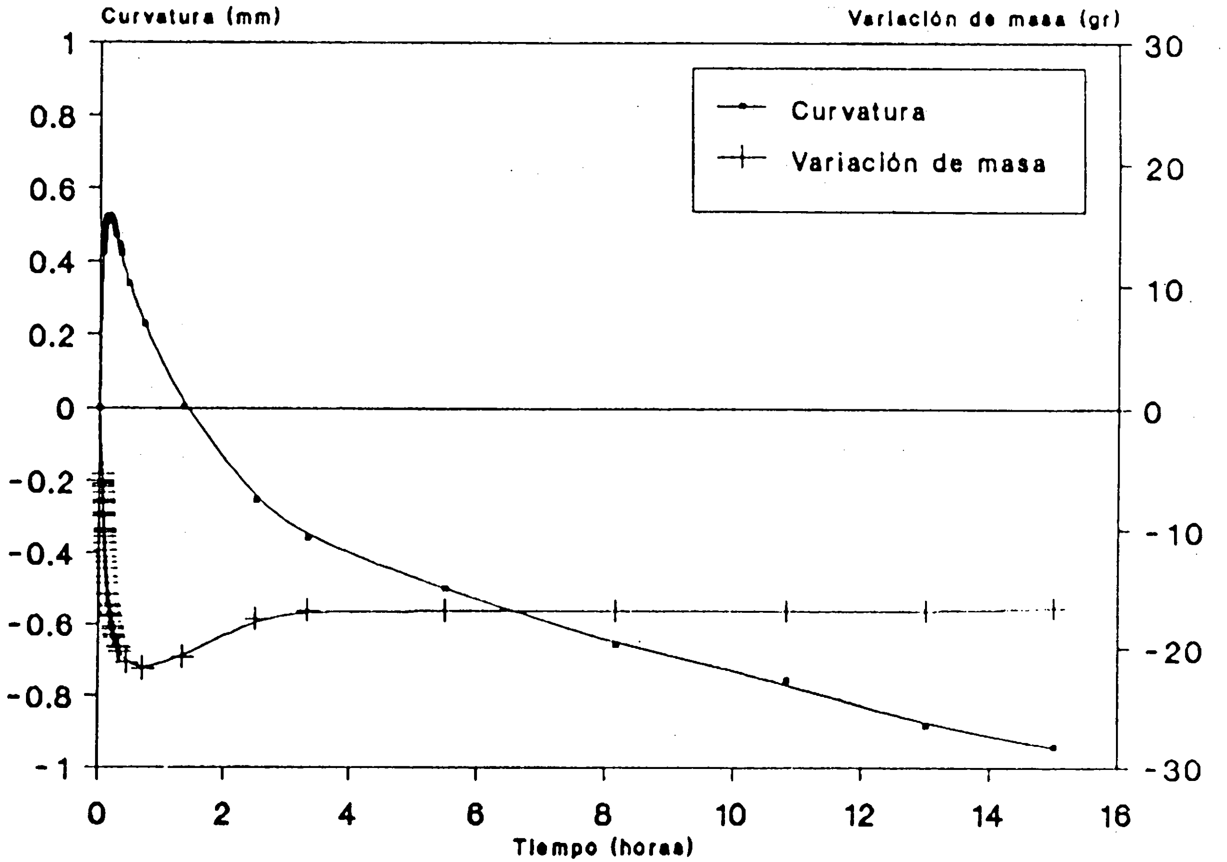


Figure 6.- VARIATION CURVATURE/MASS WITH THE TIME
APPLICATION 0'026 gr/cm2 OF WATER

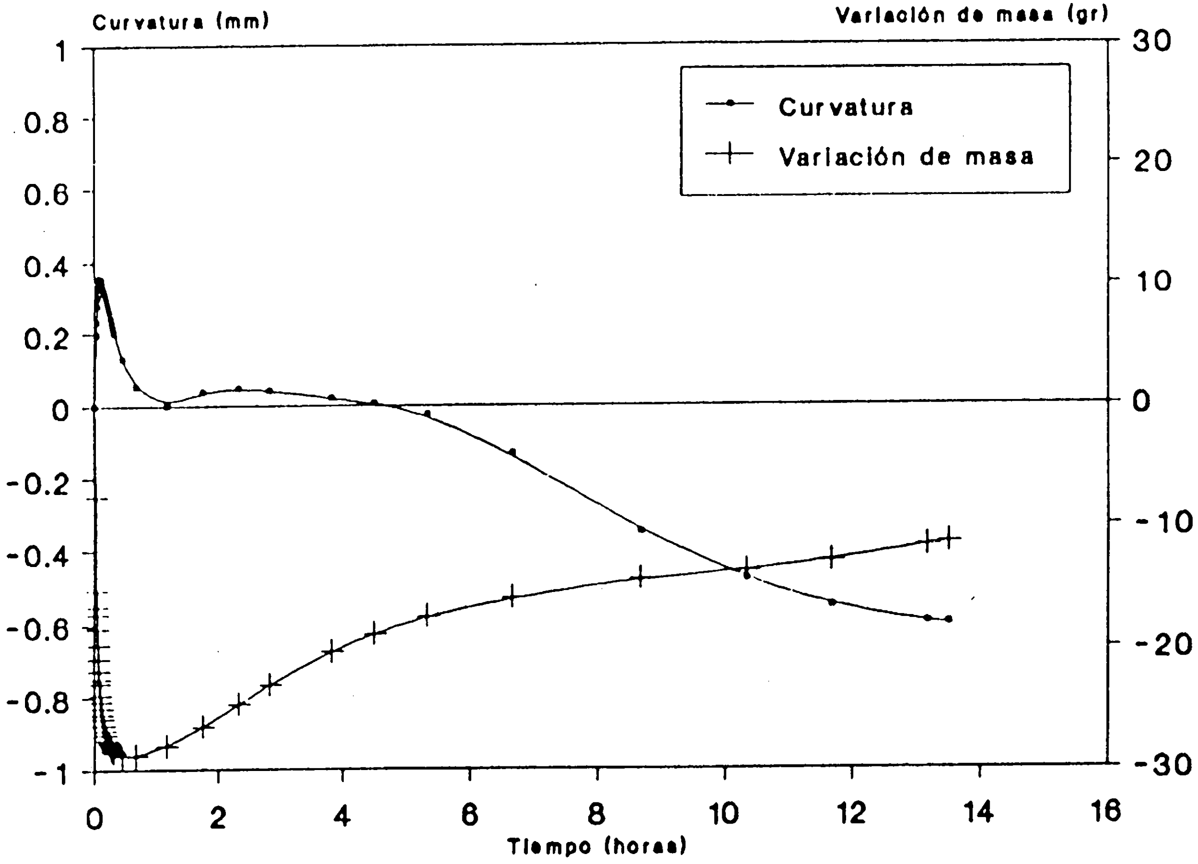


Figure 7.- VARIATION CURVATURE/MASS WITH THE TIME
APPLICATION 0'026 gr/cm2 of K2Co3 50:100

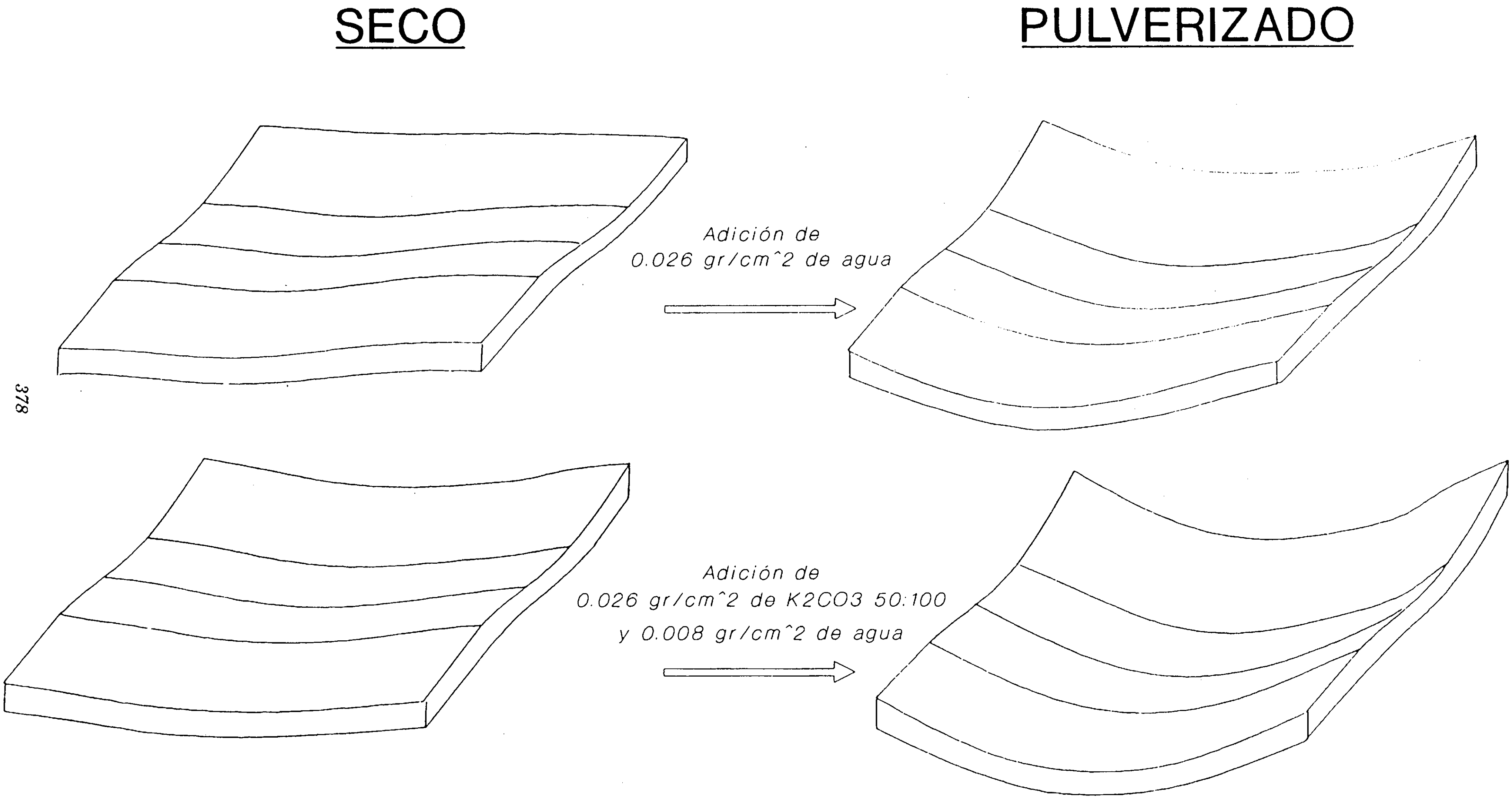


Figure 8.- CURVATURE OF THE PIECES IN THE SEQUENCE DRY-SPRAYED

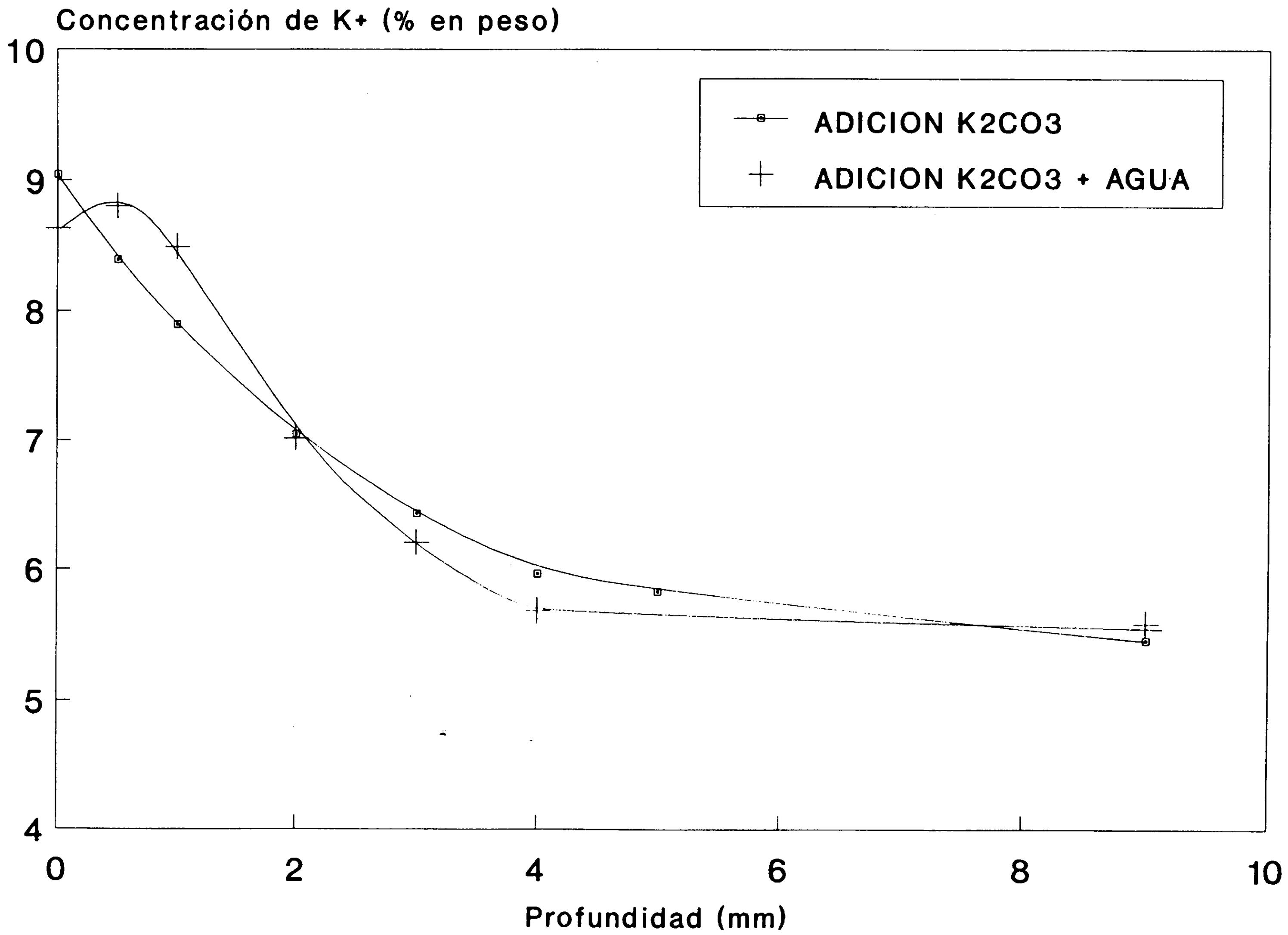


Figure 9.- PROFILE OF THE K+CONCENTRATION, UNFIRE PIECES

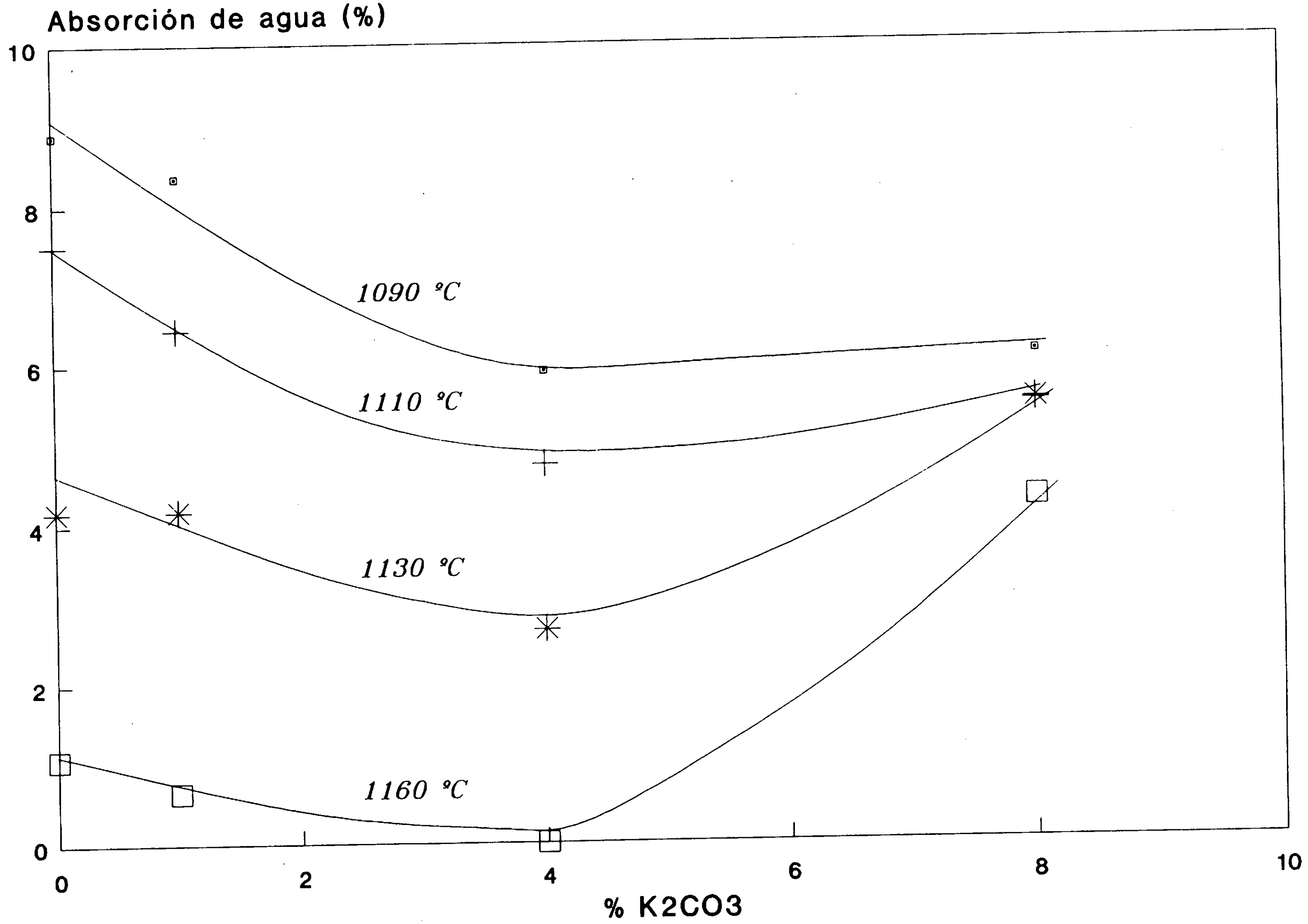


Figure 10.- VARIATION OF C. LINEAR SHRINKCAGE FOR DIFFERENT ADDITIONS OF K2CO3

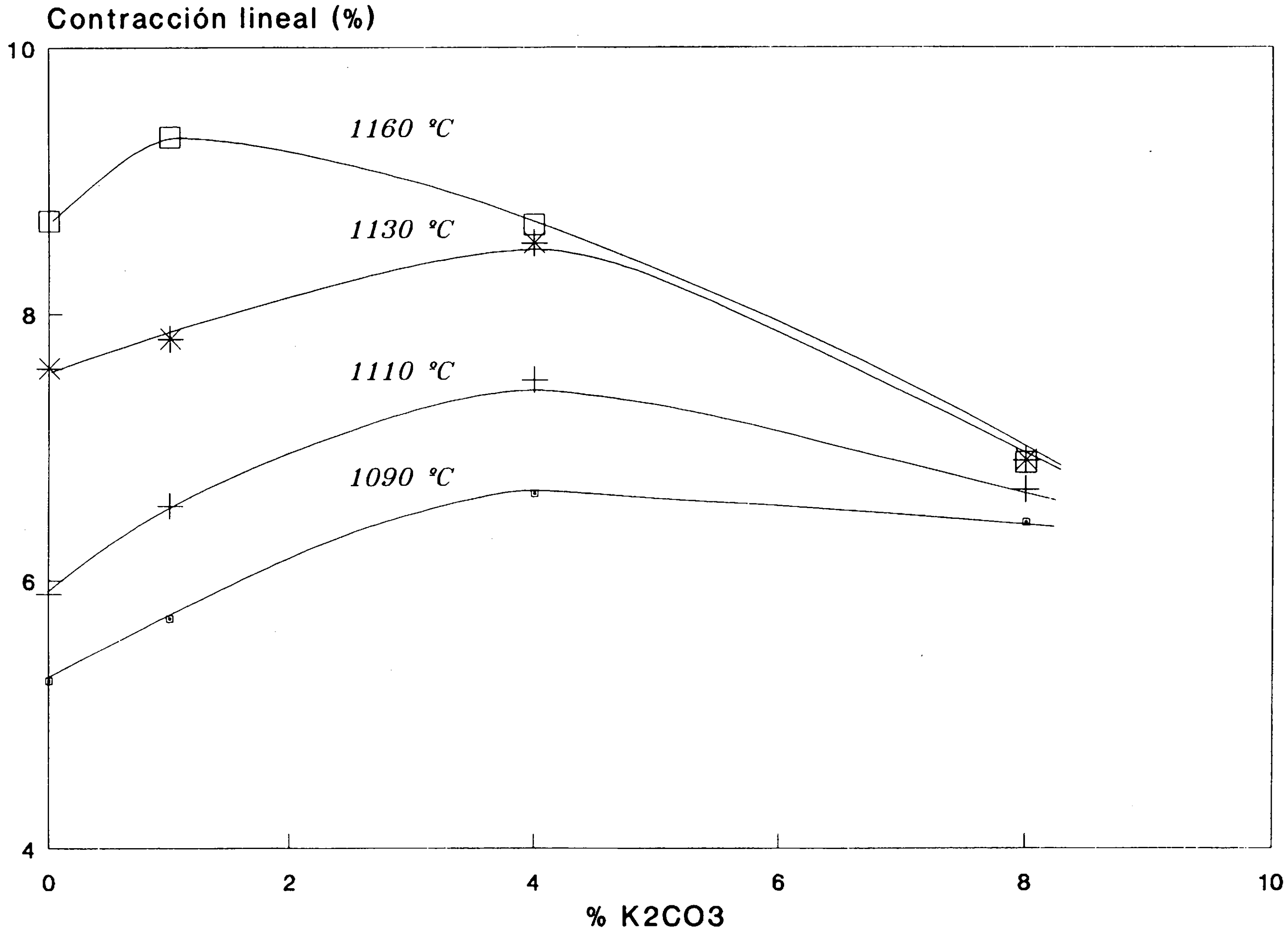


Figure 11.- VARIATION OF THE WATER ABSORPTION FOR DIFFERENT ADDITIONS OF K2CO3

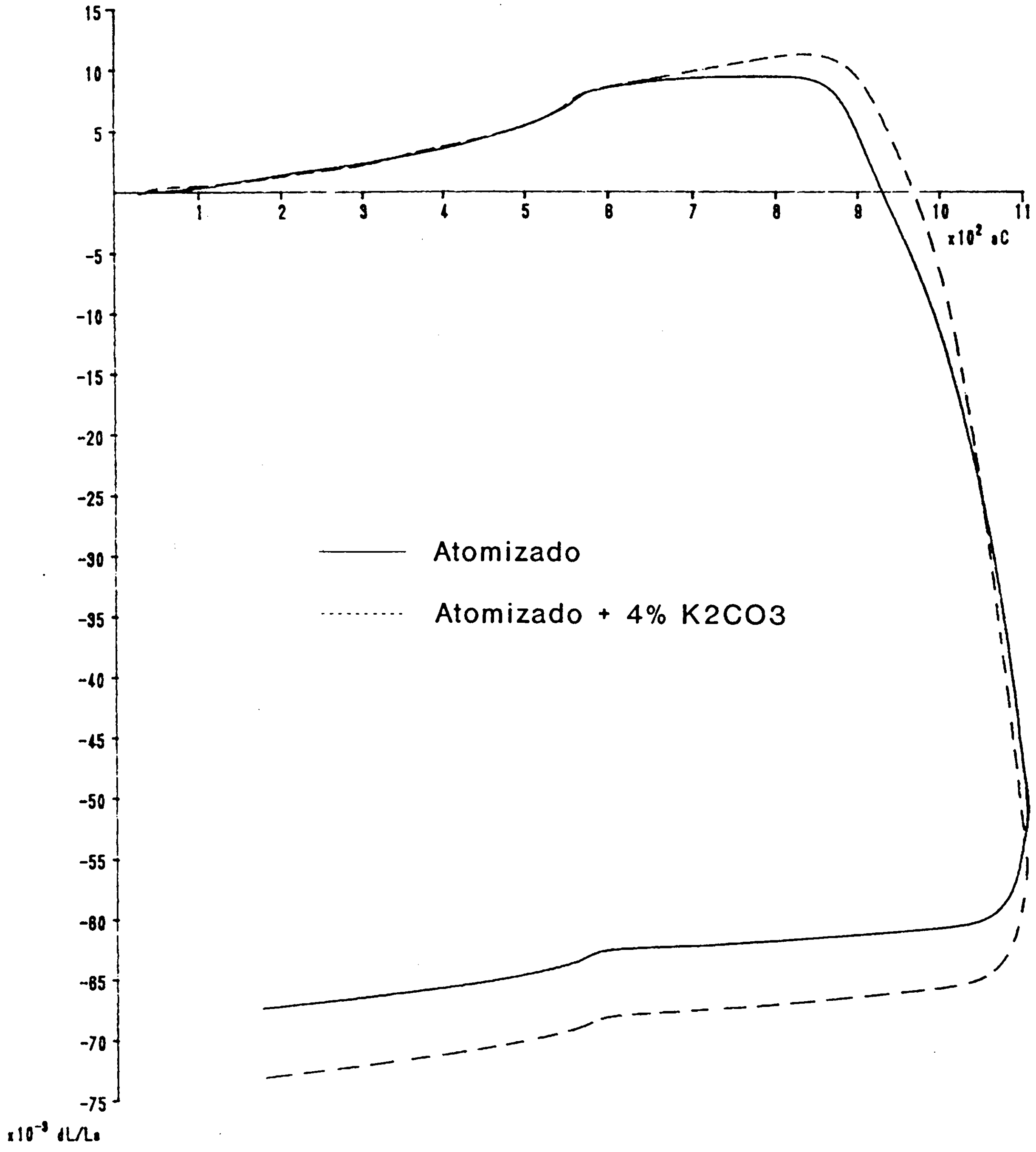


Figure 12.- DILATOMETRIC ANALYSIS

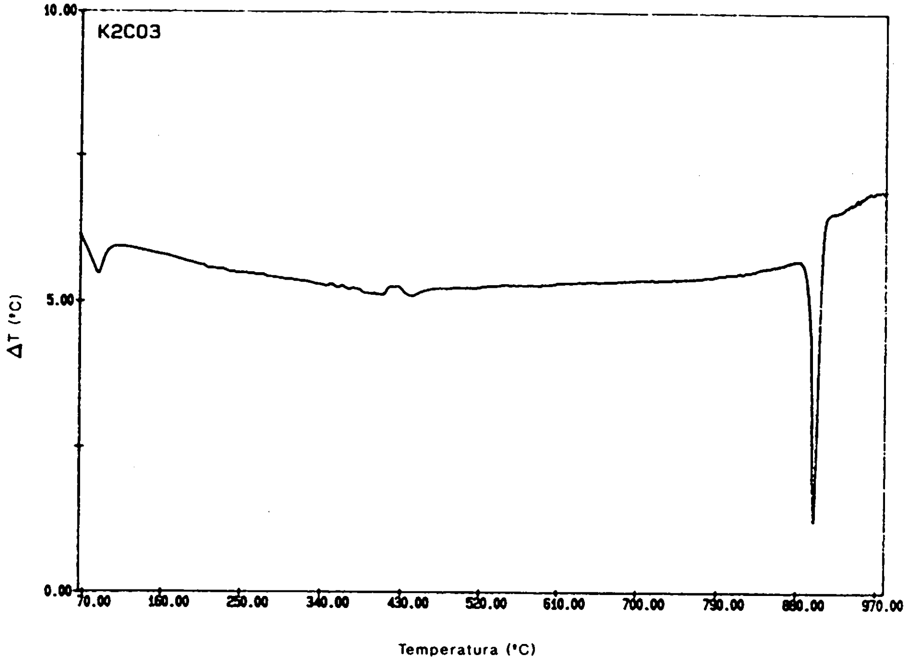
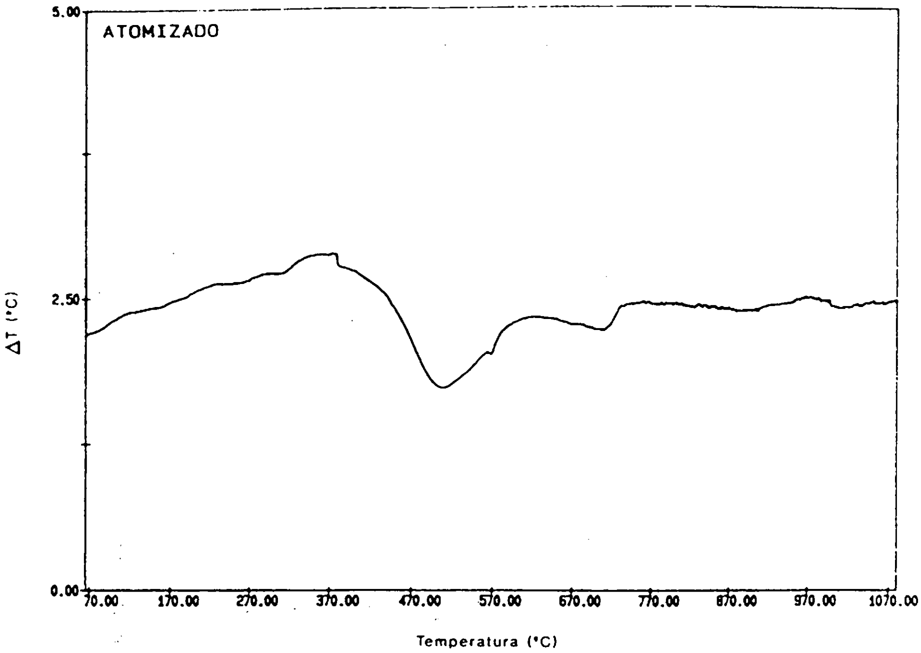
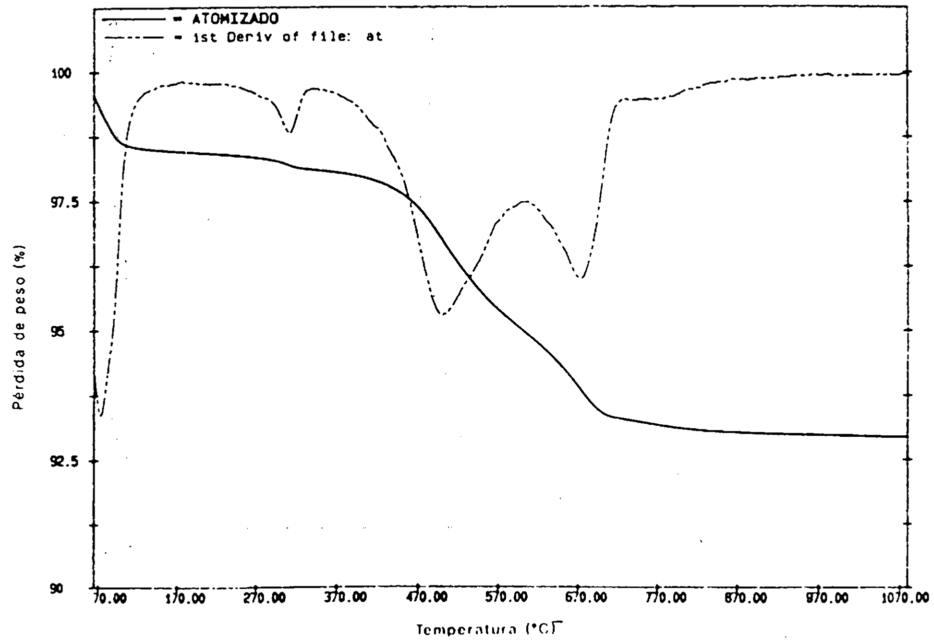


Figure 13.- THERMAL ANALYSIS DIFFERENTIAL OF K2CO3

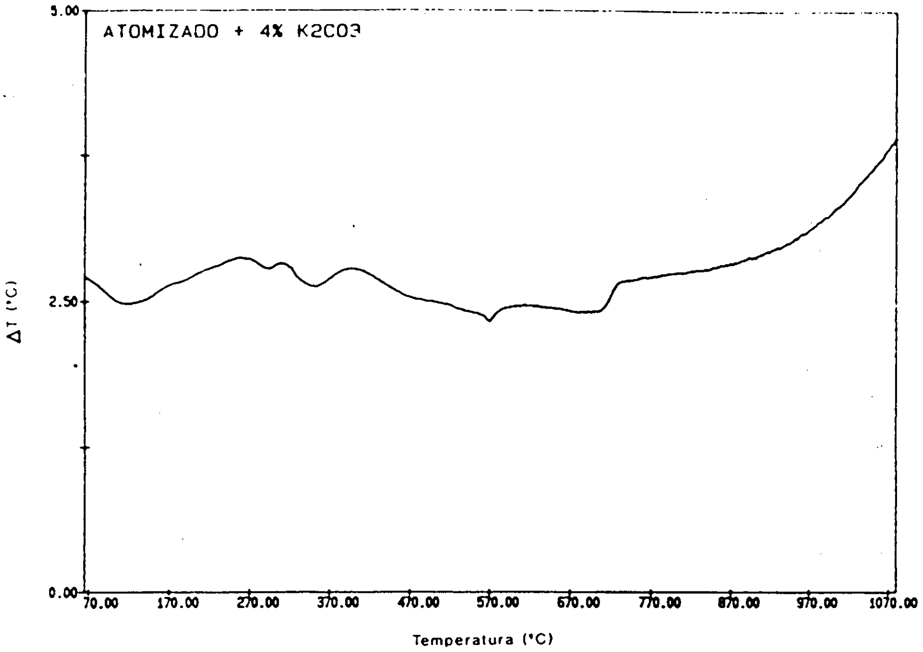


Análisis térmico diferencial

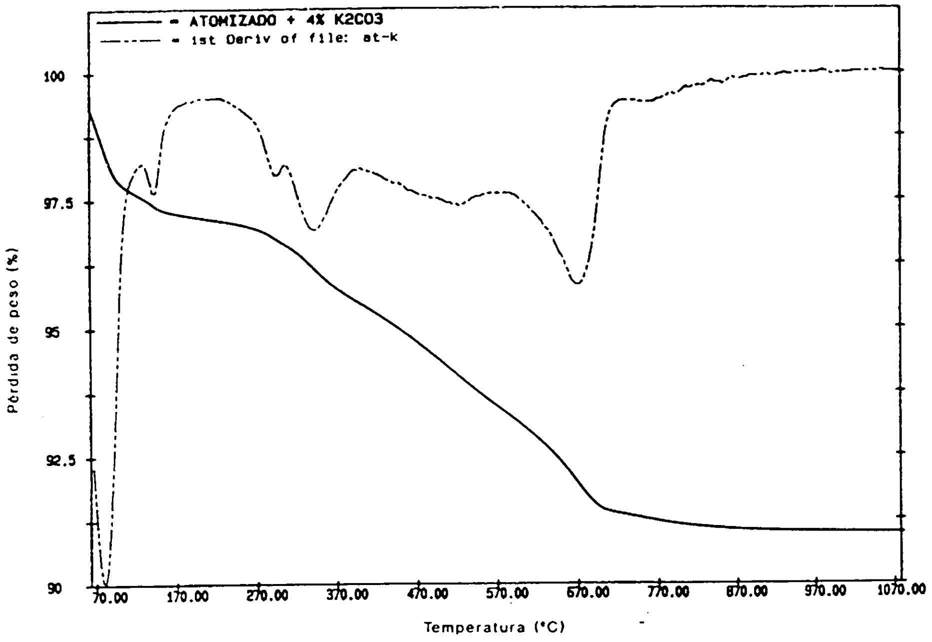


Análisis termogravimétrico

Figure 14.- A.T.D. AND T.G. OF SAMPLE 1.



Análisis térmico diferencial



Análisis termogravimétrico

Figure 15.- A.T.D. AND T.G: OF SAMPLE 3.

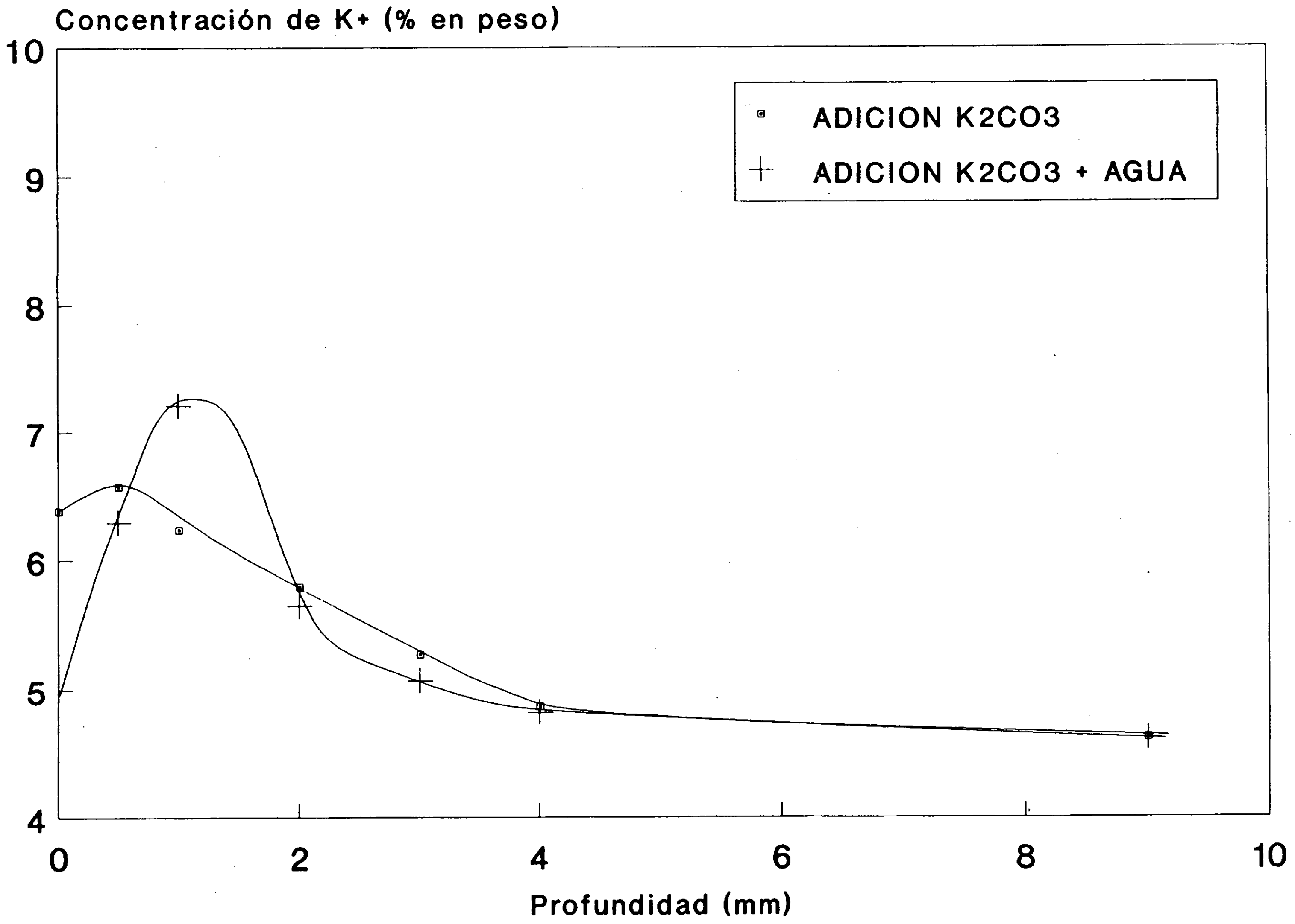


Figure 16.- K+ CONCENTRATION PROFILE FIRED PIECES

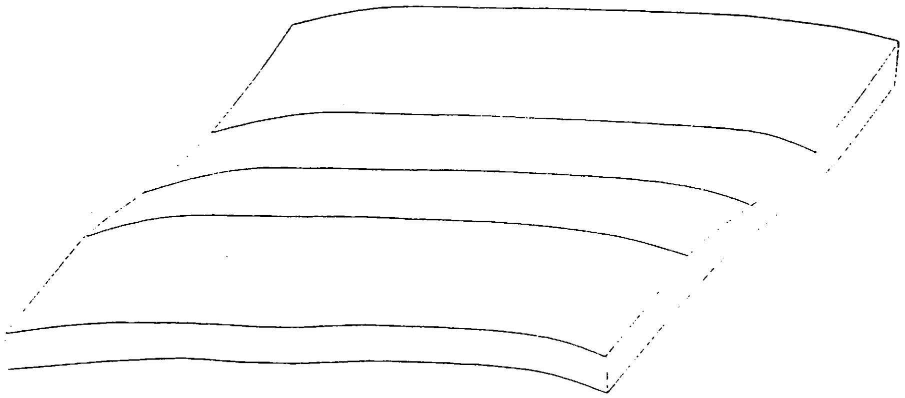


Figure 17.- CURVATURE IN FIRED TILE (0.026 gr/cm2 of water)

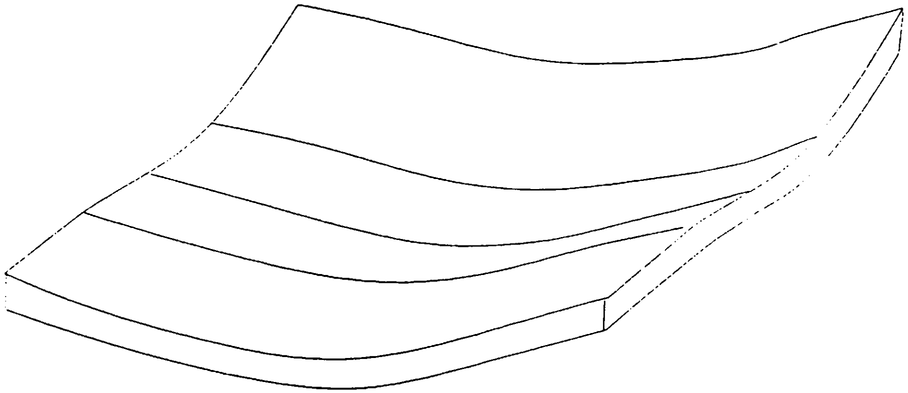


Figure 18.- CURVATURE IN FIRED TILE (0,026 gr/cm2 of dissolution 50:100 (k2CO3:water)

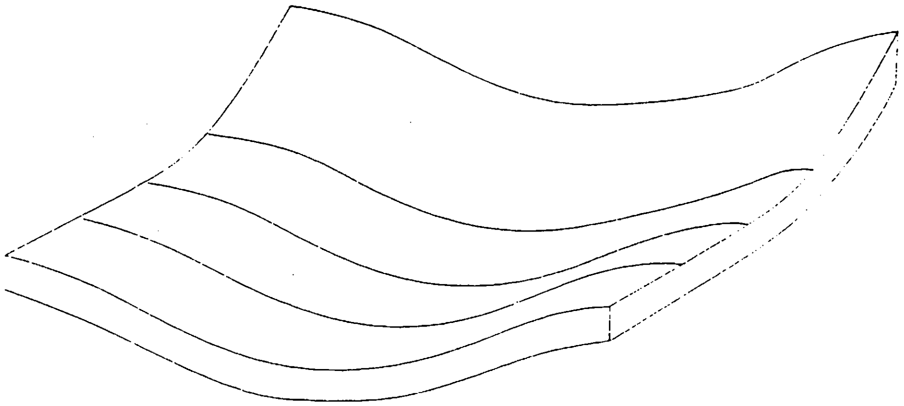


Figure 19.- CURVATURE IN FIRED TILE (0,026 gr/cm2 of dissolution 50:100) (K2CO3: water) and later addition of 0'008 gr/cm2 of water.

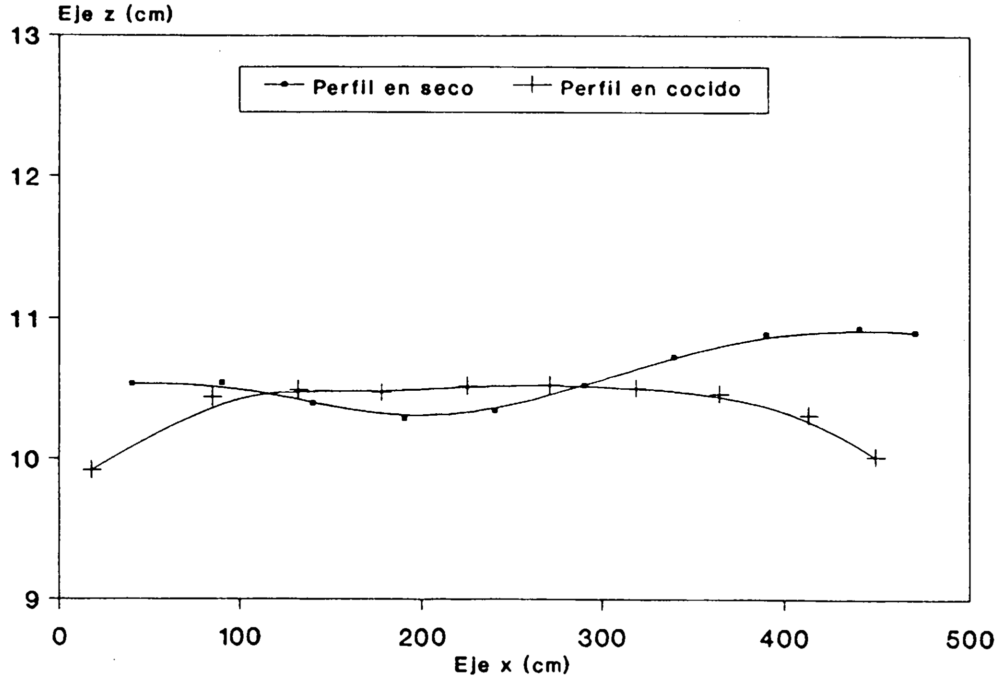


Figure 20.- COMPARISON OF PROFILES DRY/FIRED.
Application of water (coordinate Y=22.5).

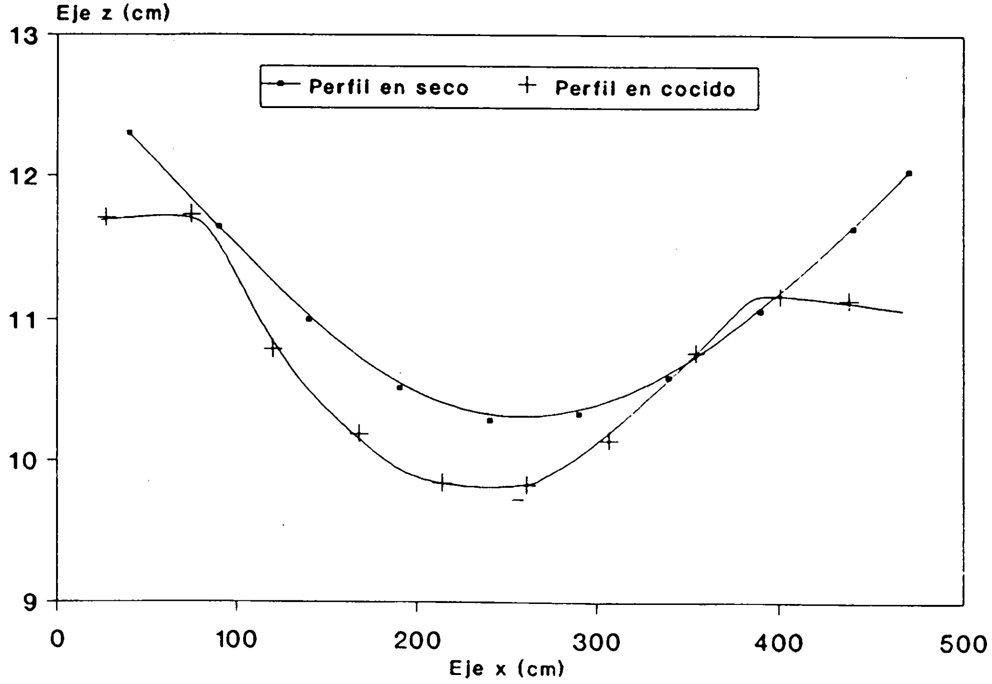


Figure 21.- COMPARISON OF PROFILES DRY/FIRED.
Application of K2Co3 (coordenate Y=22.5.)

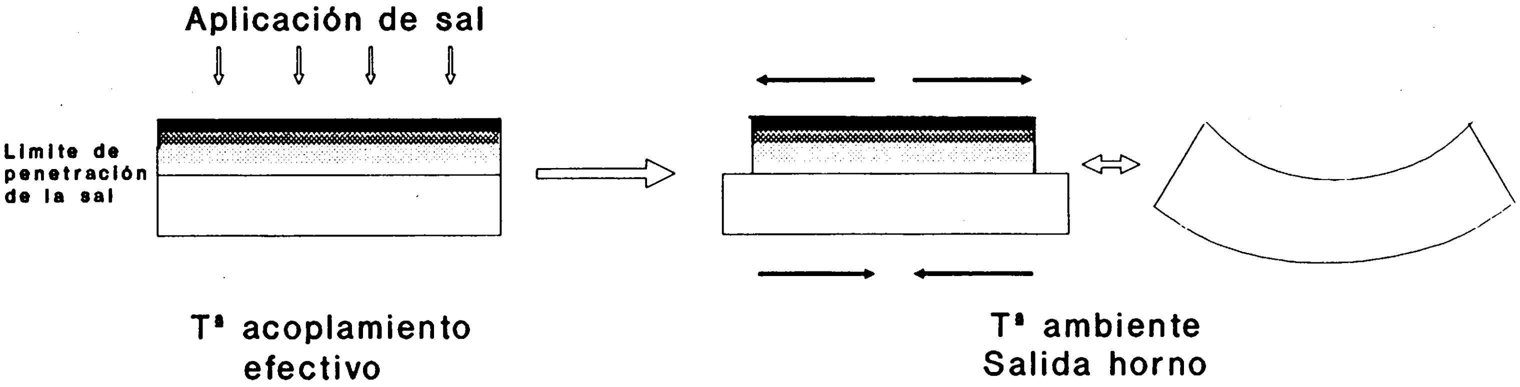


Figure 22.- THE EFFECT OF THE SUPPORTS CURVATURE IN FIRING

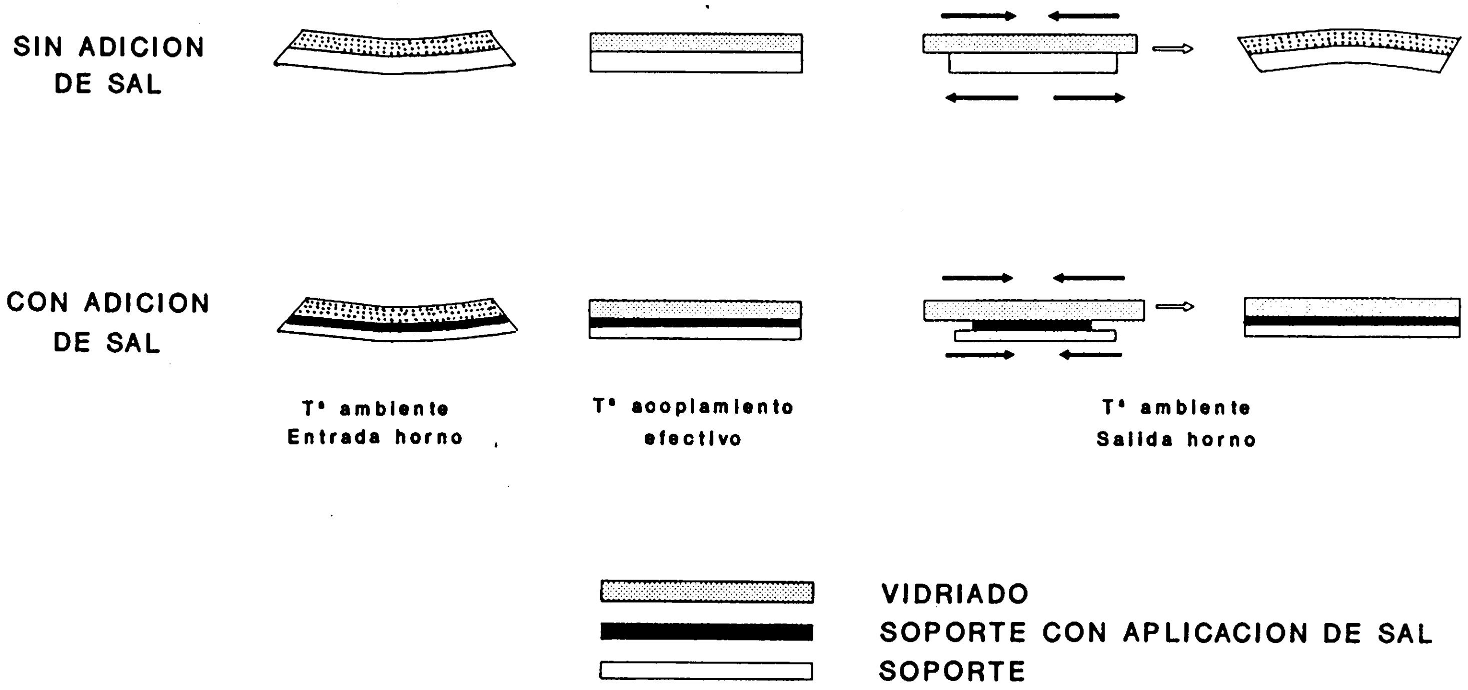


Figure 23.- EVOLUTION OF THE CURVATURE OF THE TILE DURING FIRING