SINGLE-FIRED CERAMIC WALL TILE MANUFACTURE

by Dr. Agustin Escardino Benlloch (Spain)

- University Chair of Chemical Engineering since 1965. Currently at the Jaume I University of Castellón.
- Director of the University Institute of Ceramics Technology and Director of Research of the Ceramics Industry research Association (A.I.C.E.)
- Founder of the University Institute of Ceramiscs Technology.
- Has directed 31 doctoral theses and 52 degree projects, with 88 articles on research published and 43 reports at congresses.
- Participates in several institutions devoted to the encouragement of research and science both withing and benyon the Comunidad Valenciana; belongs to several professional and research associations both national and international.

1. INTRODUCTION

European standard EN 87 classifies ceramic tile in different groups based on the shaping method used and the water absorption capability of the finished product (Table I).[1]

SHAPING METHOD	GROUP I $E \leq 3\%$	GROUP IIa $3\% < E \leq 6\%$	GROUP IIb $6\% < E \leq 10\%$	GROUP III $E > 10\%$
A	Group AI EN 121	Group AIIa EN 186	Group AIIb EN 187	Group AIII EN 188
B	Group BI EN 176	Group BIIa EN 177	Group BIIb EN 178	Group BIII EN 159
C	Group CI	Group CIIa	Group CIIb	Group III

E = Water absorption.
A = Extrusion.
B = Dry pressing.
C = Casting.

Table I.- Classification of ceramic tile according to its corresponding product standards and groups.

Single-fired wall tiles are shaped by dry pressing (moisture content 4 to 6%), and water absorption of the fired ware usually lies above 12%. They are therefore to be included in Group BIII according to the above-mentioned standard.

A series of specifications have been established in European standards which ceramic tile properties must comply with, according to the Group they belong to. These specifications may be brought together under three headings:

a) Appearance and dimensional characteristics.

Surface quality is related to the uniformity of the tiled surface, with regard to both its dimensions as well as its appearance (chromatic colour, planarity, etc.).

This is why all dimensional differences among the ware which somehow alter or hinder design harmony and planarity of the tiled surface, spoiling the overall visual and tactile effect, are considered defects, such as differences in facial dimensions (differences in sizes), wedging (lack of rectangularity) or lack of straightness in edges or sides of the ware.

Lack of chromatic uniformity in the ware, as well as the presence of other surface defects of the glaze (pinholing, stains, etc.) also diminish tile surface quality.

Surface quality and dimensional characteristics are specified in European standard EN 98. Tolerances permitted for ceramic tile belonging to Group BIII are detailed in Table II.

CHARACTERISTICS	GROUP BIII (S = Surface area in cm^2)			
	$S \le 250$	$250 < S \le 500$	$500 < S \le 1000$	$S > 1000$
Length and width Permitted deviation in % of the mean size of a wall tile with regard to nominal manufacturing size.	±0.75 for sides ≤12 cm			
Permitted deviation in % of the mean size of a wall tile with regard to the mean size of 10 samples.	±0.5 for sides >12 cm			
Thickness Permitted deviation in % of the mean thickness of a wall tile with regard to nominal manufacture size.	±0.5 mm	±0.5 mm	±0.7 mm	±0.8 mm
Straightness of edges Permitted deviation of the maximum value in % related to manufacturing size.	±0.3	±0.3	±0.3	±0.3
Rectangularity Permitted deviation of the maximum value in % related to manufacturing size.	±0.5	±0.5	±0.5	±0.5
	±0.3 for wall tile with spacers			
Planarity Permitted deviation of the maximum value in % of manufacturing size: a) Central curvature related to the diagonal. b) Edge curvature related to the length. c) Warpage related to the diagonal.	a) +0.5/-0.3 (+0.8/-0.1 mm) b) +0.5/-0.3 (+0.8/-0.1 mm) c) ±0.5 (±0.5 mm)			
Surface quality Percentage of wall tiles without defects in the lot examined.	≥95	≥95	≥95	≥95

Table II.- Dimensional characteristics and surface quality (EN 98)

b) Physical properties

Table III lists the physical properties commonly used to characterize ceramic tile, as well as the standard to be complied with in each case.

Apparent porosity of the body, measured as its water absorption capability, is one of the most significant tile characteristics as it is used to classify tile in different groups as described above, and because this conditions its applications to a great extent. There is besides a close relationship to other properties of the finished product, such as firing shrinkage, mechanical strength, moisture expansion, etc.

Wall tile with a high porosity (E >10%) is required to have mechanical strength values over 15 N/mm for thicknesses of under 7.5 mm. For greater thicknesses, the lower bound required is a little less (12 N/mm).

The only physical properties of ceramic tile that depend solely on the glaze are scratch hardness, abrasion resistance and crazing resistance. In the case of ceramic wall tile, the first two properties are of no great importance, given its application.

Standard	Property	Group BIII
EN 99	Water absorption (wt %)	>10
EN 100	Modulus of rupture (Nw/mm^2)	≥15 for e≤7,5 mm(*) ≥12 for e>7,5 mm
EN 101	Surface hardness (Mohs scale)	≥3 (Wall tile)
EN 154	Abrasion resistance	Of little importance for wall tile.
EN 103	Coeff. of linear thermal expansion from ambient T to 100°C (x10^{-6} K^{-1})	≤9
EN 104	Resistance to thermal shock	Resistant
EN 105	Crazing resistance	Resistant
EN 202	Frost resistance	Not applicable to this group of tiles

(*) e = Total tile thickness.

Table III.- Physical properties.

c) Chemical properties

These only refer to the glazed tile surface which must not undergo any appreciable change in appearance as a result of common houshold chemicals (ammonium chloride, detergents, sodium hypochlorite, etc.). The standard (EN 122) with regard to resistance by the glaze to acids (hydrochloric and citric) and alkalis (potassium hydroxide) need not necessarily be strictly complied with in the case of glazed ceramic wall tile in most of its applications.

On the other hand, the glazed surface must not be permanently impaired by the action of colouring agents (resistance to staining). It is an absolute requirement that stains produced by colouring agents (potassium permanganate and methylene blue) on wall tile be completely removed by water or detergents (EN 122).

2. SINGLE-FIRED CERAMIC WALL TILE

2.1 Evolution of the single-firing method.

Single firing is the name given in the ceramic industry to a procedure which involves subjecting the unfired glazed ware to only one thermal cycle and directly obtaining the finished product.

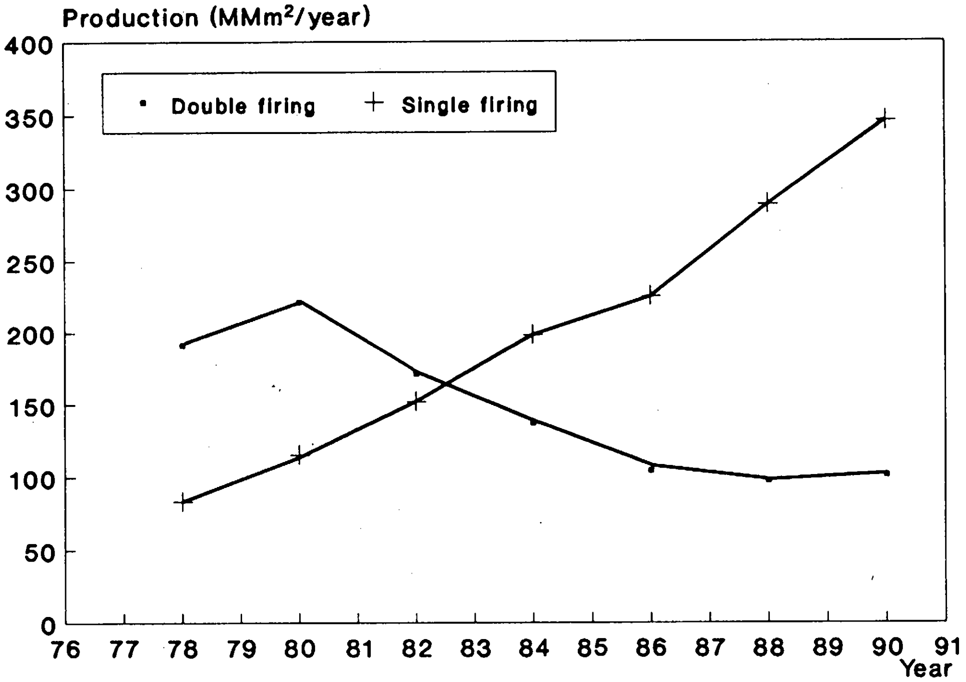
The evolution this technique has gone through in its application to ceramic tile in general is explained below, highlighting very briefly the periods during which different better-known varieties hereof were used [2].

- Single firing of small-sized tile in batch kilns: For decades.
- Single firing in tunnel kilns: At the beginning of the seventies. Duration of the firing cycle: 15-20 hours.
- Single firing in single-layer kilns on batts: During the seventies. Duration of the firing cycle: 3-5 hours.
- Fast single-firing in single-layer roller kilns without batts: Mid seventies. Duration of the firing cycle: 2-3 hours.
- Fast porous single firing with shrinkage in single-layer roller kilns: Mid seventies. Duration of the firing cycle: 50-80 min.
- Fast porous single firing without shrinkage in single-layer roller kilns: From 1983-'84 to the present day. Duration of the firing cycle: Under 50 min.

2.2 Comparative study of double-fired and single-fired ceramic tile production.

Over the last ten years there has been a clear drop in double-fired ceramic tile production and a spectacular growth of single-fired production in the ceramic wall and floor tile industry.

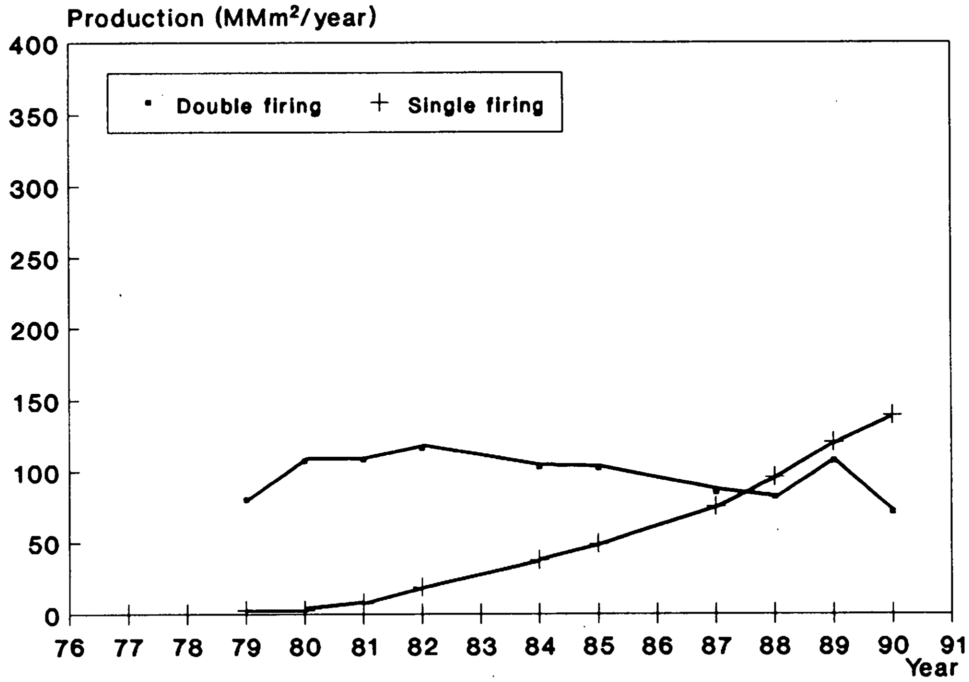
The graph in Figure 1 plots the evolution of Italian tile production (wall and floor tiles) by both procedures. In this figure, the rapid growth of single-fired production since 1978 may be observed, which in 1990 almost quadruplicates double-fired production.



Year	Double firing	Single firing
1978	191	83
1980	221	115
1982	171	152
1984	137	198
1986	104	225
1988	97	289
1990	101	346

Figure 1.- Evolution of single-fired and double-fired production in Italy.

Figure 2 reports the plot for Spain, according to figures provided by ASCER. In this case as well, a marked rise in single-fired production is to be observed since 1981, which becomes more striking from 1987 onwards and in 1990 almost doubles double-fired production.



Year	Double firing	Single firing
1979	80	3
1980	107	3
1981	108	8
1982	116	19
1984	103	38
1985	102	49
1987	85	75
1988	82	96
1989	107	120
1990	71	139

Figure 2.- Evolution of single-fired and double-fired production in Spain.

In 1990 Italian single-fired tile production was approximately 2.5 times that of Spain, whilst double-fired tile production was 1.42 times greater.

In Italy double-fired tile production begins to drop in 1980. It slowly begins to decrease in Spain in 1982.

Single-fired tile production becomes greater than double-fired tile production in Italy in 1983. This phenomenon takes place four years later in Spain.

The increasing use of the single-firing technique to the detriment of double firing in Spain may be attributed to the following two reasons:

a) The continuously augmenting use of single-layer roller kilns in which heat is transferred more rapidly and uniformly to the ware. The simultaneous firing of body and glaze can therefore be carried out in relatively short time intervals, with lower energy consumption and greater effectiveness. This guarantees a well-conducted single-firing process with high production.

b) The progressive application of the single-firing technique to porous wall tile manufacture. Its influence begins to take on importance in 1986, as a result of which the problems of high shrinkage of the body on firing, which were encountered initially, are gradually overcome.

2.3 Characteristics of single-fired wall tile.

These are virtually the same as in traditional or fast double-fired tile manufacture. The only difference lies in the manufacturing method and therefore in some of the raw materials used (especially the glaze).

The intervals in which the most significant finished product characteristics lie in this kind of tile are listed below (obtained by the above-mentioned standard test methods). This information stems from the files of the Test Laboratory For The Finished Product of the Asociación de Investigación de las Industrias Cerámicas (AICE).

- Water absorption (EN 99): 15-16.5%
- Modulus of rupture (EN 100): 20-228 N/mm
- Mohs scratch hardness (EN 101): 3-5
- Crazing resistance (EN 105): Resistant (*)
- Chemical resistance (EN 122):

In general, glazes with a matt finish are usually attacked quite easily by hydrochloric acid, only slightly by citric acid and are resistant to potassium hydroxide. Glossy glazes on the contrary, are more resistant to attack by acids and more vulnerable to alkali attack, although the latter is generally less intense than that by acids on matt glazes.

3. DESCRIPTION OF THE MANUFACTURING PROCESS

Figure 3 shows a single-firing process scheme in which the two possiblities of wet or dry pressing powder preparation are both considered [3].

a) Dry grinding

Dry grinding is usually carried out in pendulum mills, where powder is obtained with a considerable amount of fines (80% < 60 μm) and a coarse fraction (larger than 200μm) under 5%.

The powder obtained is lightly wetted and granulated to achieve grain-size distribution suitable for developing the pressing stage in the best possible conditions.

After adjusting its moisture content to 4-6%, the granules are transferred to storage arks and left to stand to homogenize their moisture content. They are screened immediately before pressing to remove oversize agglomerates.

b) Wet grinding

This grinding method is at present the most commonly utilized in single-fired wall tile manufacture.

(*)Single-fired wall tile glazes are generally resistant to the standard crazing test. However, many craze when subjected to more intensive treatment.

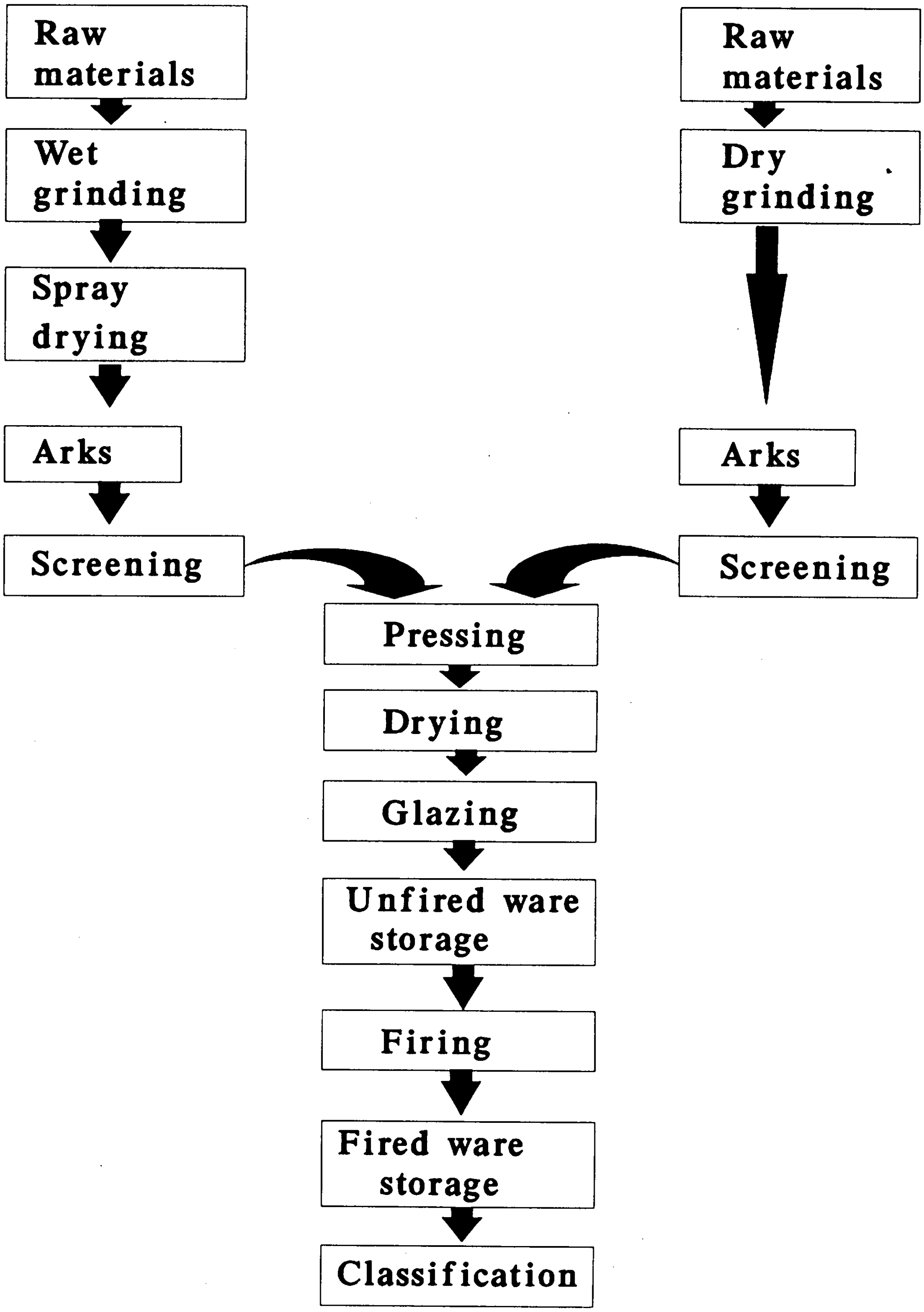


Figure 3.- Standard production plant for single-fired tile

The different clays making up the composition are homogenized and stored in separate arks. They are then crushed to 30 mm. The mix is gravimetrically proportioned and charged in ball mills, with water and deflocculants, in suitable proportions. The solids concentrations used range between 65 and 70 % (in wt). Deflocculants are used in order to increase solids concentration in the suspension.

A previous study of the rheological behaviour of the slip is required to determine the optimal proportions of solids and water, as well as the kind and amount of deflocculant to use.

On reaching the desired grain-size distribution, the suspension resulting from the ball mill is put through a vibrating screen to remove particles with sizes over 125-200 µm. It is then transferred to a spray-drying facility where more or less spherical and hollow particle agglomerates are obtained with very suitable characteristics for conducting the pressing operation.

Keeping the moisture content of the spray-dried powder virtually constant at the spray-dryer outlet is advisable as variation in the moisture content influences compaction of the pressed pieces, which affects the properties of the fired ware.

The spray-dried powder is stored in arks for some days to achieve a uniform moisture content, both inside each granule as well as between different-sized granules.

The spray-dried powder is screened before pressing at 1000 µm mesh aperture, with a view to removing all possible impurities and/or aggregates formed by spray-dried granules stuck together.

c) Comparison of the two grinding methods.

We believe wet grinding offers some technical advantages with regard to dry grinding. The most important are listed below: [4]

(i) The different constituents of the raw materials used in obtaining the pressing powder utilized in shaping the body are homogenized better.

(ii) The grain-size distribution of the primary particles is finer than by dry grinding. On reducing the coarse particle fraction, pressing powder reactivity increases owing to a greater specific surface area. As a result, lower firing temperatures are required.

(iii) The spray-dried powder granules have a greater flow rate than those obtained by dry grinding with subsequent wetting, and therefore distribute more rapidly and uniformly in the pressing dies. This favours the pressing operation since it allows production of the shaped ware to rise on the one hand, while on the other improving compaction uniformity in the green ware, which entails a greater uniformity of the finished product.

However, certain economic disadvantages are involved, viz.:

(i) Greater outlay for the facilities.

(ii) Greater expenditure in preparing the pressing powder owing to the use of deflocculants and the added energy consumption in spray drying.

It is, as always, necessary to weigh up the advantages and disadvantages when decisions are to be taken. We consider wet grinding to be preferable to dry grinding in the present state of technology.

d) Pressing

Shaping of the ware is carried out by unidirectional dry pressing (moisture content 4-6%), generally in hydraulic presses. Aim of the pressing, besides shaping the ware, is to provide the ware with enough mechanical strength (6-10 kg/cm) to withstand transport to the dryer.

e) Drying

The recently shaped ware is placed in a continuous dryer where its moisture content is reduced to 0.5-1% (dry basis), in order to increase mechanical strength and virtually reach a suitable moisture content for feeding the ware into the kiln.

The drying cycle does not usually last longer than 120 min.

f) Glazing

On removing the ware from the dryer at a temperature of over 70°C, it is covered with raw glaze in the glazing line.

The most commonly used technique in glazing single-fired wall tile is bell or waterfall-curtain glazing with high density glaze slip to avoid formation of entrapped bubbles. At present, dry glazing is also conducted for certain models or effects.

It is vital to strictly control glaze application and intensify monitoring of the glazed surface before firing as, owing to the use of very short firing cycles, the glaze has little time to flow and cover the defects caused by inadequate application.

g) Firing

Fast single-firing of the glazed ware is at present conducted in single-layer roller kilns without batts. In these kilns the ware is fired in one layer and is borne directly by the rollers. As heat is transferred to the ware in these kilns more rapidly and uniformly, considerably shorter firing cycles (less than 45 min) can be used than were required when the ware was supported on batts or set in several layers.

Single-layer roller kilns offer certain advantages besides allowing shorter firing cycles. In fact, less energy is consumed per square meter manufactured tile and greater firing flexibility and uniformity is provided, among others. This has all led to its rapid implementation in the ceramic wall and floor tile sector.

4. CONSIDERATIONS ON THE RAW MATERIAL OF THE BODY

Wall tile is a product requiring high dimensional stability. This is obtained by starting with a composition which undergoes very little shrinkage on firing. On the other hand, the product must possess considerable porosity (12-14%), which provides it with good adherence on laying and less weight per square meter.

High porosity of the body gives water access to its interior, either by ambient moisture adsorption or by liquid suction during or after laying, therefore allowing hydration of the vitreous and amorphous phases contained in it. This hydration can lead to expansion of the body of the fired ware and cause curvature or crazing of the glaze.

All this makes it necessary for the fired ware to bear a minimal fraction of amorphous phases and a considerable proportion of crystalline phases as crystalline phase formation lowers shrinkage on firing.

4.1 Starting compositions

Suitable porosity of the fired body and reduction in shrinkage of the ware on firing is achieved by introducing calcium carbonate with or without magnesium carbonate in the starting composition. Furthermore, during the firing, the magnesium and calcium oxides produced by the decompostion of these carbonates, react with the amorphous phases resulting from the dehydration of the clay minerals, forming magnesium and/or calcium aluminosilicates, which are stable in the face of moisture activity.

Normally, the greater the calcium carbonate content of the starting composition, and the more refractory the minerals it bears, the more reduced is the variation in linear shrinkage and water absorption, with temperature, in the interval close to peak firing temperature as may be observed in Figure 4. In this graph, linear shrinkage curves and water absorption versus maximum firing temperature are compared of a composition for fabricating stoneware, of two others based on the same composition to which 3 and 6% (in wt) calcium carbonate were added, as well as another standard composition commonly used in single-fired wall tile manufacture.

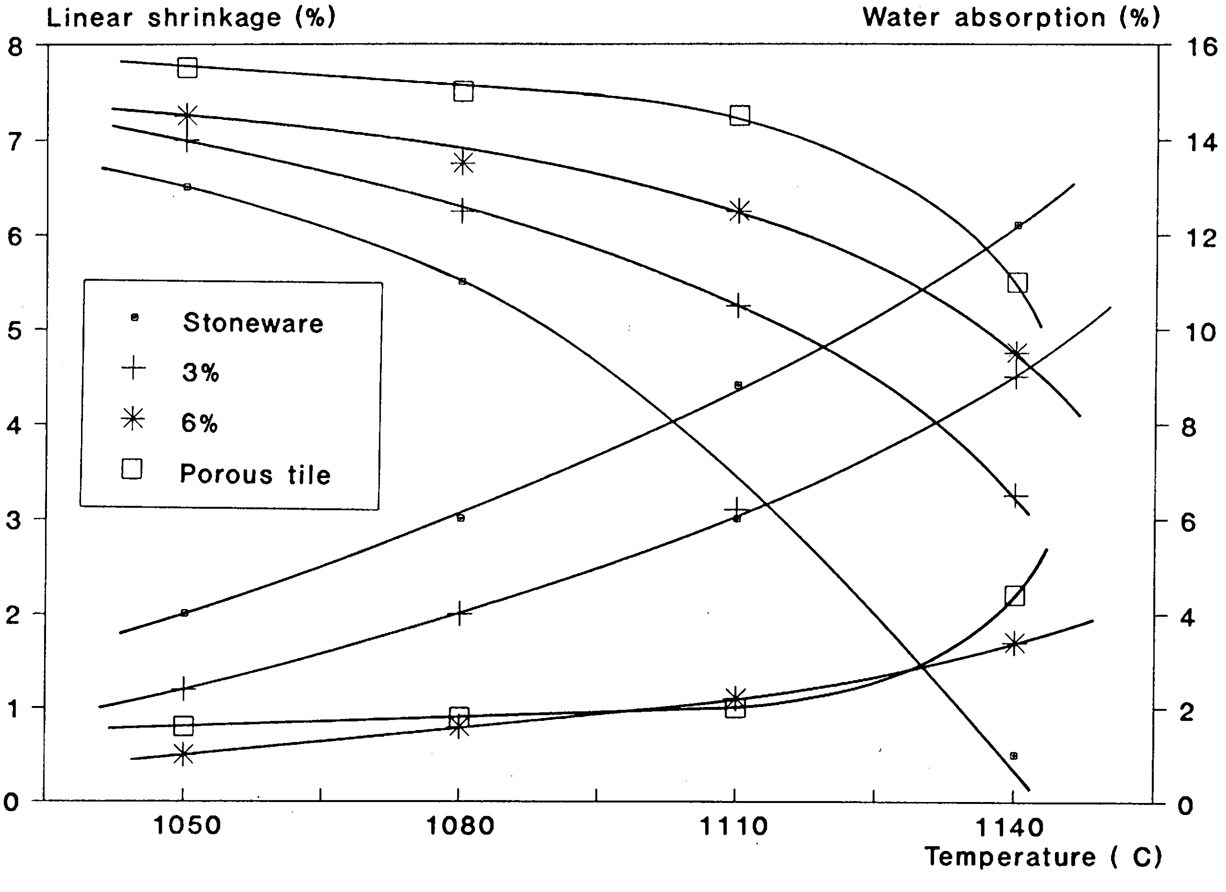


Figure 4.- Variation of water absorption and linear shrinkage in terms of carbonate content.

The recommended carbonate content in starting compositions normally ranges from 10 to 16 %. If less, the proportion of crystalline phases obtained during firing is too low, leading to greater shrinkage of the ware than would be desirable, making it possible for differences in facial sizes and thickness as well as wedging to develop because of small temperature gradients in the kiln, and also for the fired ware to become more hydratable and therefore expand more by moisture adsorption.

Use of a carbonate content percentage above that indicated could be detrimental to the mechanical properties of the fired body, owing to the porosity of the resulting ware possibly becoming excessive. Futhermore, decomposition of the carbonates could not be fully accomplished during the preheating stage owing to the short firing cycles being used, thus creating an added problem.

On the other hand, as expressed in other research papers [5], and as may be observed in Figure 5, the single-fired porous ware undergoes quite a noticeable shrinkage in the preheating zone, between 800 and 900°C, owing to the reaction between the amorphous phases (produced by the decomposition of the clay minerals) and the calcium oxide (from the calcite). It is therefore not advisable for the calcium carbonate content to be too great, since this shrinkage becomes more accentuated as the calcium carbonate content increases and the non-plastic materials content drops in the starting composition.

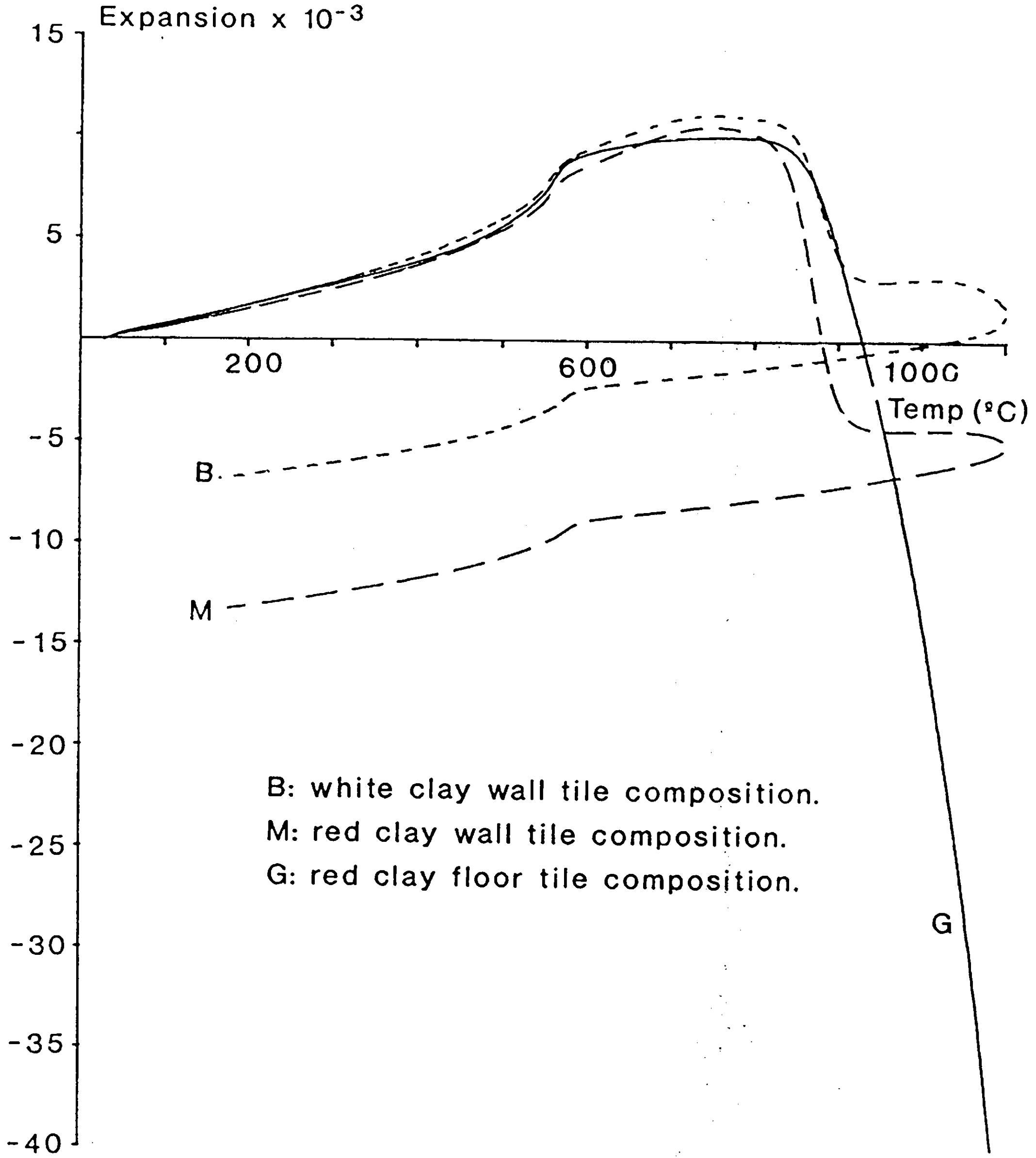


Figure 5.- Dilatometric curves of the compositions B, M and G.

It may be concluded from the foregoing that optimizing the percentage of carbonates and other mineral species present in the composition (quartz, clay mineral, etc.) by means of dilatometric analysis is advisable, to try and reduce shrinkage of the ware as much as possible in the preheating interval and in the firing temperature interval.

In Figure 5, the dilatometric curves corresponding to a red clay (M) and a white clay (B) composition, chosen at random among those commonly used as raw material for fabricating single-fired wall tile, are plotted. Similarly, the curve corresponding to a composition for obtaining red stoneware is also plotted for comparison. In the curves corresponding to the first two compositions, the temperature variations in the working zone (1050-1110°C) may be seen to hardly affect the change in size of the test pieces (a 10°C temperature variation invloves dimensional variation of 0.05-0.10%). The G curve on the contrary undergoes a great change in this region.

If the composition used is suitable for achieving low shrinkage during firing, the differences in compaction which may arise in pressing because of pressure fluctuations or pressing moisture content, hardly affect the size of the ware. In these compositions, a variation in bulk density of 0.05 g/cm^3, equivalent to a change in pressing pressure of about 50 kg/cm , entails a shrinkage modification during firing of only 0.1%.

Finally, it is worth mentioning that the composition must bear an adequate amount of fluxing clay minerals (which give rise to alkaline oxides), in order to enable the necessary amount of vitreous phase to form for the ware to achieve adequate mechanical strength.

The compositions normally used in the fabrication of single-fired wall tile vary in function of the body colour required. Some considerations follow on the compositions to be used for single-fired wall tile made of red or white clay.

a) Red clay body

In fabricating this kind of body, a mix of natural clays is generally used as raw material, which contains iron oxide, in amounts ranging from 4-8% (expressed as Fe_2O_3, in wt), and variable quartz and carbonate contents, until the desired properties are obtained (Tables IV and V). At times, small amounts of non-plastic materials (sand, flock, etc.) are added to reduce shrinkage during firing.

The red clays normally used in factories in the Valencian Community are reported in Table IV.(*)

Clay	Carbonates (%)	Iron (%)	Quartz	Plasticity
Araya	35-40	4-5	+	+
Sichar	25-35	4-5	++	++
Mas Vell	25-35	4-5	+++	++
Chulilla	6-14	6-7	+	+
Galve	<3	6-7	++	++
Villar	<3	6-7	++	++
Moró	<3	6-7	+++	——

Table IV

In Table V some commonly used compositions are detailed:

Clay	Type 1	Type 2
Araya	--	--
Sichar	--	--
Mas Vell	35-45	25-35
Chulilla	--	20-50
Galve	30-50	--
Villar	--	--
Moró	5-20	0-15

Table V

(*) The characteristics and composition of these clays may be found in several studies published by the Instituto de Tecnología Cerámica [6] [7]. The percentages are wt%.

The TG and DTG curves corresponding to a composition of this kind are plotted in Figure 6. In the DTG curve the minimum values corresponding to weight loss may be observed, as a result of: loss of physically adsorbed moisture, the possible decomposition of organic material, dehydroxylation moisture loss and carbonate decomposition, in sequence as temperature rises.

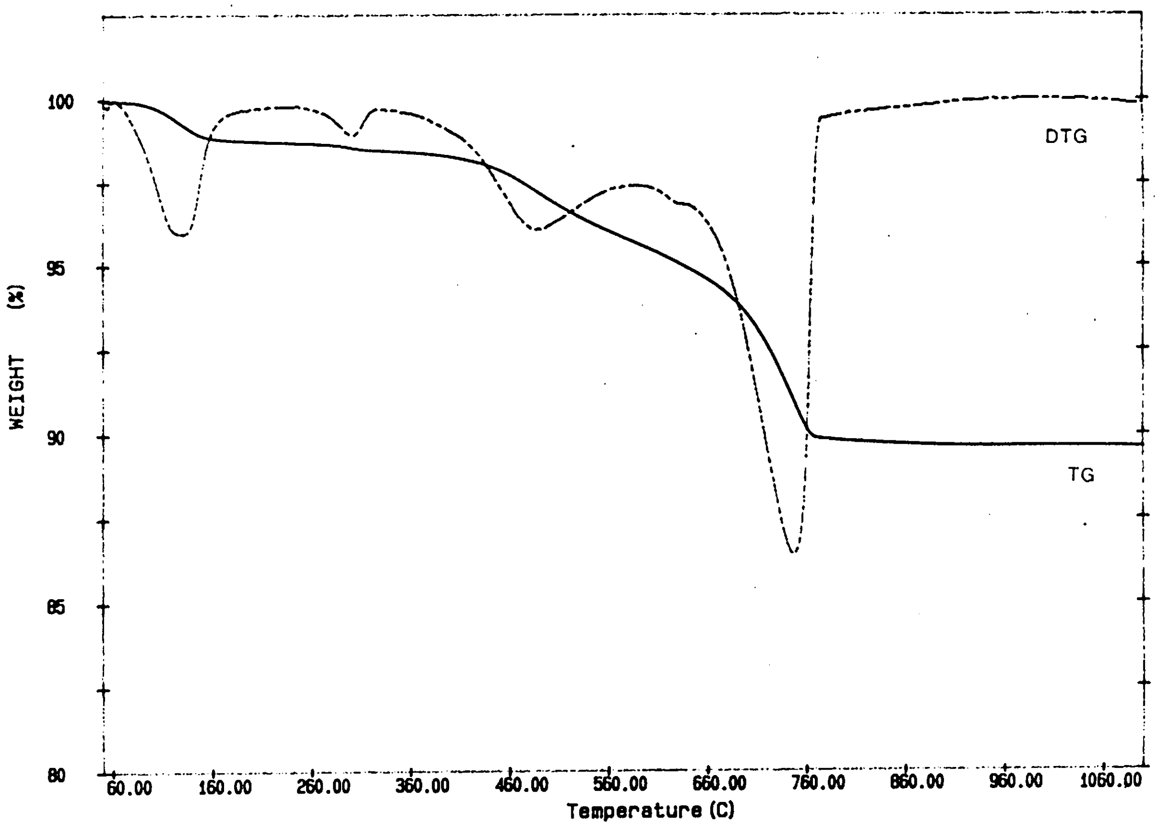


Figure 6.- TG and DTG of a red clay wall tile composition

b) White clay body

To obtain this kind of body, a starting mix of clays with a low iron and carbonate content is used (Table VI), to which a certain amount of non-plastic material is added (to reduce shrinkage during firing). Calcium carbonate is likewise added (Table VII) so that the carbonate content will be that required for the fired piece to be sufficiently porous and for the crystalline phases to form in suitable amounts.

Kaolin is sometimes added in varying amounts to obtain the degree of whiteness desired in the body.

The factories in the industrial area of the Valencian Community usually use the raw materials listed in Table VI.

Clay	Carbonates (%)	Iron (%)	Quartz	Plasticity
Imported clays	-	<1,5	++	+++
Spanish clays	-	1,5-3	+++	++
Kaolins	-	<0,5	+	++

Table VI

In Table VII, some standard commonly used compositions are detailed.

Clay	Type 1	Type 2
Imported clays	45-55	25-30
Spanish clays (Teruel)	--	20-30
Kaolin	0-10	0-10
Calcium carbonate	10-15	10-20
Sand	0-5	0-5

Table VII

The TG and DTG curves corresponding to a composition of this kind are plotted in Figure 7. In the DTG curve the minimum values corresponding to weight losses may be observed, as a result of: loss of physically adsorbed moisture, the possible decomposition of organic material (almost negligible in this case), dehydroxylation moisture loss and carbonate decomposition, in sequence, as temperature rises.

4.2 Characteristics of the pressing powder and the particles forming it.

It is useful to distinguish between grain-size distribution of the primary particles which form the pressing powder and are the grinding product, and the granules (particle agglomerates) whose structure depends on the grinding method used (wet or dry method) and on the procedure used in obtaining them (wetting facility, shredder, or spray-dryer).

a) Grain-size distribution of the pressing powder granules.

It is of interest to point out first of all, the differences with regard to shape and density found in the granules obtained by the different pressing powder elaboration methods.

The density of the grains obtained by spray drying is always considerably lower than those obtained by dry grinding with subsequent granulation by wetting. Furthermore, whilst density of the

---

(*) The characteristics and composition of these clays may be found in several studies published by the Instituto de Tecnología Cerámica [7] [8]. The percentages are wt%.

latter increases slightly with size, density of the former decreases. This is due to the fact that the spray-dried granules bear internal craters and holes which grow in volume with the size of the granule, contrary to the solid ones obtained by dry grinding. Particle packing in the spray-dried granules is less compact than in that obtained by wetting, which also contributes to lower density.

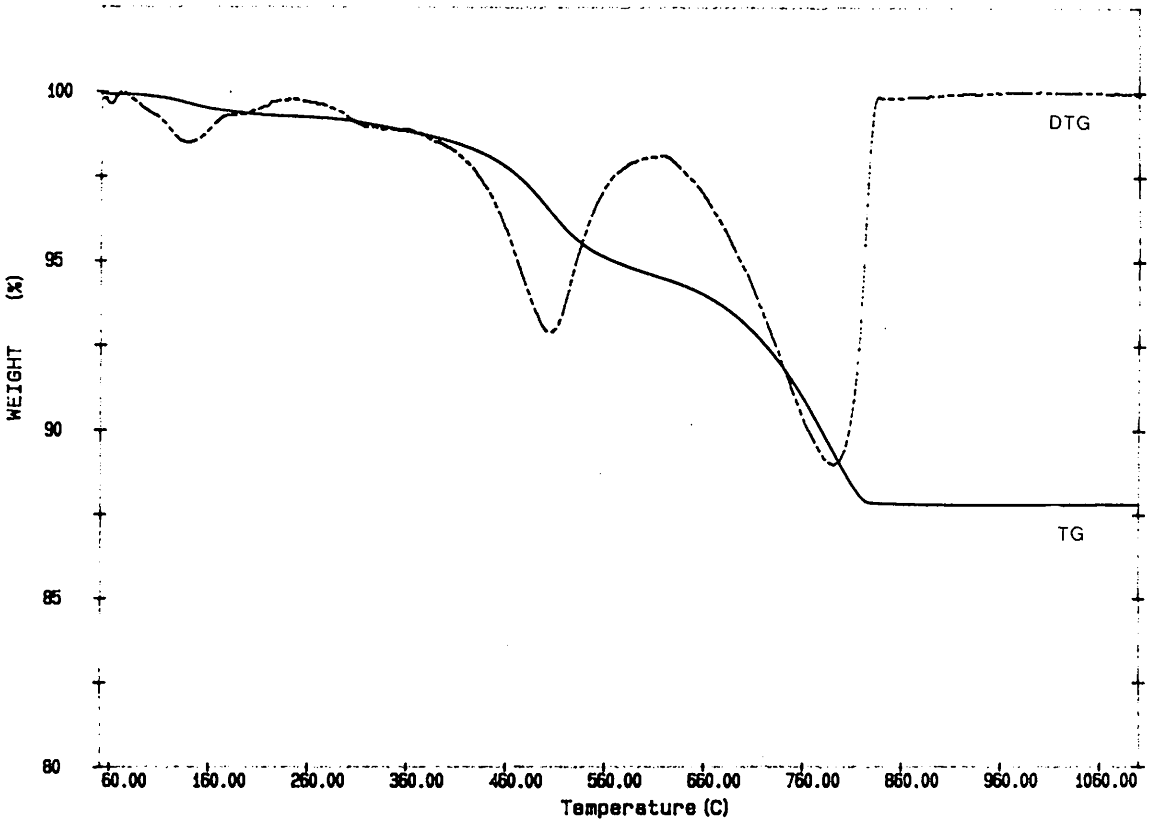


Figure 7.- TG and DTG of a white clay wall tile composition

This is why the ware pressed from powder prepared by dry grinding, although it may at times have a greater bulk density (at the same pressing pressure) than spray-dried powder, usually involves more drawbacks on drying and shrinks less on firing.

Pressing powder obtained by the dry method (using traditional methods (pendulum or hammer mill and wetting facility), is formed by irregularly formed granules, whilst that obtained in a granulator has a more or less spherical shape. Spray-dried powder is always made up of hollow spherical particles.

Granule shape influences the pressing operation. The more spherical the granules are, the better they flow, thus facilitating pressing die filling. Futhermore, excess moisture found inside the granules obtained by dry grinding (wetting facility and shredder) can lead to matter sticking to the presses, thus diminishing performance in the first stage owing to the frequency with which the dies must be cleaned. The pressing powder obtained by spray-drying therefore behaves better during the pressing operation.

Pressing powder flow is also affected by grain-size distribution of the granules [9]. In general, optimal distribution in spray-dried powders should be as narrow as possible, with 55-65% in the 200 to 500 μm range. There should not be more than 15% of the granules over 500 μm in size (with a maximum of 5% over 750 μm). The presence of granule sizes under 150 μm has a detrimental effect on pressing powder flow owing to greater friction among the granules. Granule sizes over 500 μm produce the same effect, owing to their normally being agglomerates of smaller granules which lose sphericity on sticking together.

b) Grain-size distribution of the particles forming the pressing powder grains.

In order to industrially monitor size distribution of pressing powder primary particles, the following grain-size fractions are usually utilized as reference elements:

i) Rejects on a screen with 60 µm mesh aperture.

A low oversize percentage must be found on a 60 µm mesh aperture screen to obtain good particle reactivity, which guarantees complete breakdown of the carbonates present and reaction between the earth oxides, formed with the decomposition of the corresponding carbonates, and the silica and alumina contained in the clay minerals. The reactivity of these components increases when particle size decreases, owing to increase of the specific surface area of the solid.

If the oversize percentage is not held above a certain limit, lower compaction of the ware may be found on pressing (at a given pressure and moisture content), which entails greater shrinkage on firing. Moreover, mechanical strength in the green ware can decrease considerably, which would mean an added drawback.

However, if the oversize percentage is too great, defects develop in the finished ware, as the coarser particles are less reactive and decompose with greater difficulty (mainly the CO_3Ca particles). Too great an oversize fraction would moreover reduce screen performance and could lower production.

The usually recommended values for the oversize fraction at 60 µm range from about 3 to 8% of the total solids treated.

ii) Grain-size fractions over 175 µm.

Based on the points made in the foregoing subsection, it is advisable for the oversize fraction at 125 µm not to be over 0.8%, since carbonate particle sizes over 125 µm lead to defects in the glaze of the ware, mainly pinholing, as more time is required for their decomposition and CO_2 continues to be released after the glaze has melted.

5. CONSIDERATIONS ON THE GLAZE

5.1 Characteristics of the glazes used.

The glaze components, which may be of a vitreous or crystalline nature, and the amounts found in the composition, determine the aesthetic and technical characteristics of the end glaze. Knowledge of the raw materials to be used and the influence they have on the physical and chemical properties of the resulting glaze, as well as the proportions in which they are mixed, is therefore of great importance in ceramic glaze formulation.

Glazes for single-fired wall tile are mainly formed by frits (either one or several mixed frits), which become part of a composition in percentages ranging from 80 to 95%, to which small amounts of crystalline raw materials are added (kaolin, zirconium silicate, etc.), to slightly modify the technical and aesthetic characteristics of the frits utilized. The frits used therefore constitute the raw materials which have the greatest influence on the performance and characteristics of the end glaze. In fact, the minimal specifications a ceramic glaze for single-fired wall tile can be asked to comply with, can quite easily be fulfilled by a vitreous material such as a frit.

The aesthetic effect of the glaze is achieved on decorating by means of silk screen printing over a glaze base layer. The most important technical characteristics of glazes for ceramic wall tile are crazing resistance and resistance to chemical attack by acids and alkalis.

Both technical characteristics can be optimized by modifying the proportions and nature of the frits used in glaze formulation, since the other raw materials which are added in small amounts have other specific purposes: kaolin is added to reduce the sedimentation rate of the suspension, zirconium silicate to increase glaze opacity, etc.

As well as the foregoing, glazes used in single-fired tile manufacture must above all, have a high melting temperature (T>950°C), to allow complete outgassing of the body (mainly CO_2 is released), whilst the glaze layer remains porous. The fused glaze must reach its minimal viscosity at a temperature of about 1100°C (maturing temperature), in order to have time to correct surface defects (especially pinholing) which may arise during the glazing operation.

The intervals in which the values of some of the most important thermal properties of glazes commonly utilized in single-fired porous tile manufacture lie, are as follows:

Coefficient of linear expansion (25-300°C): $60\text{-}70.10^{-7}$ °C^{-1}
Softening temperature: 700-790°C
Transformation temperature: 600-670°C
Sealing point: 920-980°C
Maturing temperature: ◡1100°C

5.2 Recommendable compositions

As indicated above, glazes for single-fired porous tile are mainly made up of frits to which small amounts of kaolin or zirconium silicate are added.

As glazes are required to have a high melting temperature (T>950°C), the frits used in formulating these glazes are free from or contain low amounts of alkaline oxides whose presence considerably lowers melting temperature. This is why their boron and lead content is also very low. Alkaline oxides are replaced in this instance by alkaline earth oxides (CaO, MgO) and zinc, which fuse at high temperature, forming eutectics, so that fusion takes place rapidly once begun.

The white glazes used generally contain zirconium silicate. In order to obtain glazes with a matt finish, as zirconium tends to increase viscosity of the melted glaze, it is usually replaced by calcium and zinc oxides which do not produce this effect and besides, promote phase separation during firing and therefore the formation of crystals, thus delaying fusion during the heating stage.

5.3 Glazing operation

The most commonly utilized procedure in glaze application on the body, for single-fired wall tile, is in aqueous suspension by the bell method, mainly owing to being able to use slips with quite a high density (1.85-2 g/cc). In this density interval, entrapped bubbles are less likely to form during manipulation, thus giving rise to fewer surface defects than by any other method of application. However, operating at these high densities can lead to problems in the rheology of the system, thus making it necessary to obtain a good deflocculation state by suitable additions.

Binders are required in order to promote bonding of the glaze layer to the unfired body. On the other hand, the high alkaline earth oxide content in the frits used, entails added drawbacks as a result of its solubility in water. The presence of these cations in the aqueous suspension modifies its rheological properties, so that they act as flocculants (increasing viscosity). Moreover, these dissolved cations react with the added binders, reducing viscosity of the suspension and lowering glaze bonding capability. The combination of both effects can bring about changes in the rheological behaviour of the suspension, so that when just prepared it can show a good state of deflocculation and sediment after a certain time, also diminishing adhesion to the body. The dissolution of alkaline earth cations in the slip water can, besides the drawbacks mentioned above, lead to precipitation of certain salts which can give rise to pinholing later, in the glaze.

6. CONSIDERATIONS ON THE FIRING STAGE

6.1 Firing cycle

During firing a series of physico-chemical transformations develop in the body and in the glaze as a result of which the unfired piece acquires the properties and appearance desired in the finished product.

A typical firing cycle has been plotted in Figure 8 for single-fired wall tile. Although the temperature-time curves vary in each instance, according to the starting raw materials and the characteristics of the product to be obtained, they all have about the same shape. Curves 1 and 2 in Figure 8 were plotted from temperature data obtained by means of thermocouples located throughout the kiln which operated according to a suitable thermal cycle. Temperatures were measured directly above and below the roller plane, so that real temperature variation in the ware must be approximately what is represented in curve 3.

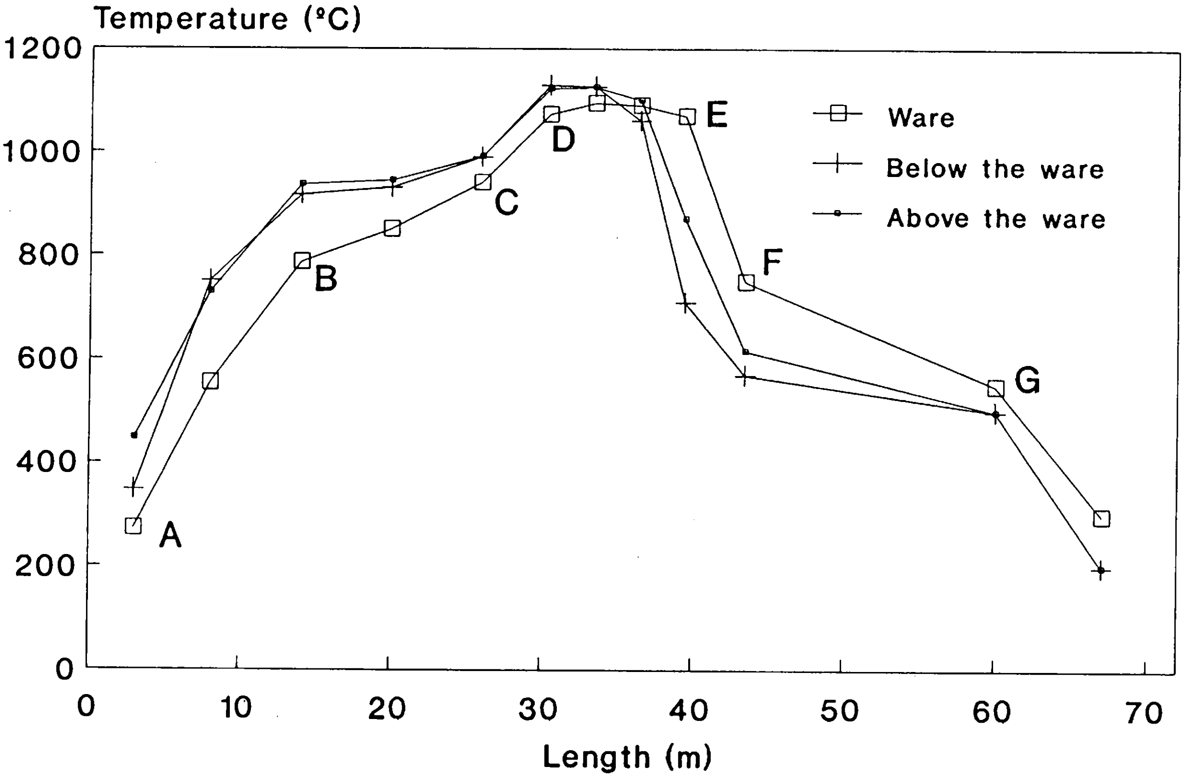


Figure 8.- Firing cycle.

The first leg of this curve (AB), corresponds to the preheating phase. Heating at the kiln entrance is established at a suitable rate to remove, without sharp jumps, moisture which may have been adsorbed by the body from the ambient, or during glazing, in order to avoid cracks forming or explosions of the ware taking place. It is advisable to install a tunnel dryer with cars at the kiln entrance to remove the moisture the body may have adsorbed after drying, in order to raise the heating rate in this zone and shorten it.

In the (BE) segment, all the physico-chemical transformations take place which turn the green ware into the end product.

In fabricating single-fired wall tile, the first part (BC) of this segment, corresponds to the most delicate period of the firing cycle. Throughout this period, during which temperature of the ware must be held at between 800 and 900°C, breakdown of the carbonates takes place as a result of which carbon dioxide is released and magnesium and calcium oxides are formed.

As the green body used for this kind of tile bears a considerable amount of carbonates, the volume of the gases released on decomposition of the carbonates is considerable. It is therefore necessary to complete their breakdown before reaching 900°C, when the glaze layer has not yet melted and remains porous, allowing CO_2 to pass through it. If carbon anhydride is still being released after fusion of the glaze, surface defects may appear in the end glaze, i.e. mainly pinholing, if the fused glaze does not manage to cover the craters produced by CO_2 bubbles passing through it, owing to the short firing times used.

In the temperature interval being considered (800-900°C), the body undergoes shrinkage [5] as a result of the partial sintering of the amorphous phases formed by decomposition of the clay materials. The higher the calcium carbonate content in the composition used, the greater the shrinkage, which may be considerably reduced by non-plastic additions.

Composition behaviour must be closely monitored in this temperature interval, as excessive shrinkage because of the above-mentioned reason can give rise to deviating facial dimensions and wedging in the finished product, even when shrinkage of the ware in the peak firing temperature region (1000-1100°C) is minimal.

When the previously described transformations have almost ended completely, heating of the ware may proceed at a greater rate (segment CD), until maximum firing temperature is reached. During this period, the alkaline earth oxides, formed by carbonate decomposition, combine with the amorphous phases mentioned above to form stable crystalline phases (magnesium and calcium aluminosilicates). Moreover, sintering of the amorphous phases continues.

It is of great importance that this period should be long enough for crystalline-phase formation to develop completely, since this contributes to maintaining the dimensional stability of the piece during firing and also for the body to acquire the desired porosity. Besides, if these reactions are not completed, the fired ware may contain hydratable intermediate amorphous phases, which can react with moisture from the ambient or from the materials used in installing the tile, thus giving rise to body expansion which would involve crazing of its glaze layer.

In the peak firing temperature zone of the kiln (segment DE), sintering of the body is completed. The complete fusion of the glaze covering it also takes place. The dwell time of the ware in these conditions must be long enough for the glaze to fuse completely, forming a uniform layer without bubbles over the body.

The last stretch of the curve (EFG) corresponds to the cooling stage. This leg breaks down into three parts: fast cooling at high temperature, an intermediate slow-cooling step and a final fast-cooling step.

The high resistance to thermal shock of fired ware at temperatures above 600°C allows rapid cooling during the first step without fractures developing (cracking) in spite of the high thermal gradient produced inside the ware. Therefore, cooling can be conducted by forced convection, with air injected at temperatures close to ambient (segment EF).

When the ware is close to 573°C (point F), temperature at which allotropic transformation of α-quartz in ß-quartz takes place, resistance to thermal shock is low, making it necessary to reduce the cooling rate considerably. In this short temperature interval, cooling of the ware in the kiln takes place almost exclusively by natural convection and radiation.

Once beyond this critical point, the ware again becomes resistant to thermal shock, so that the final cooling step can be conducted rapidly by forced convection.

6.2 Defects originating in the firing stage.

Crazing of the glaze and curvature of the ware are two of the most important defects which can arise in this stage in single-fired wall tile manufacture. Both defects stem from differences between the coefficients of expansion of the glaze and the body. It is therefore advisable to know the thermal behaviour of the raw materials to be used in order to choose the most suitable materials to obtain the best possible body-glaze fit, during the first cooling step (T>750°C).

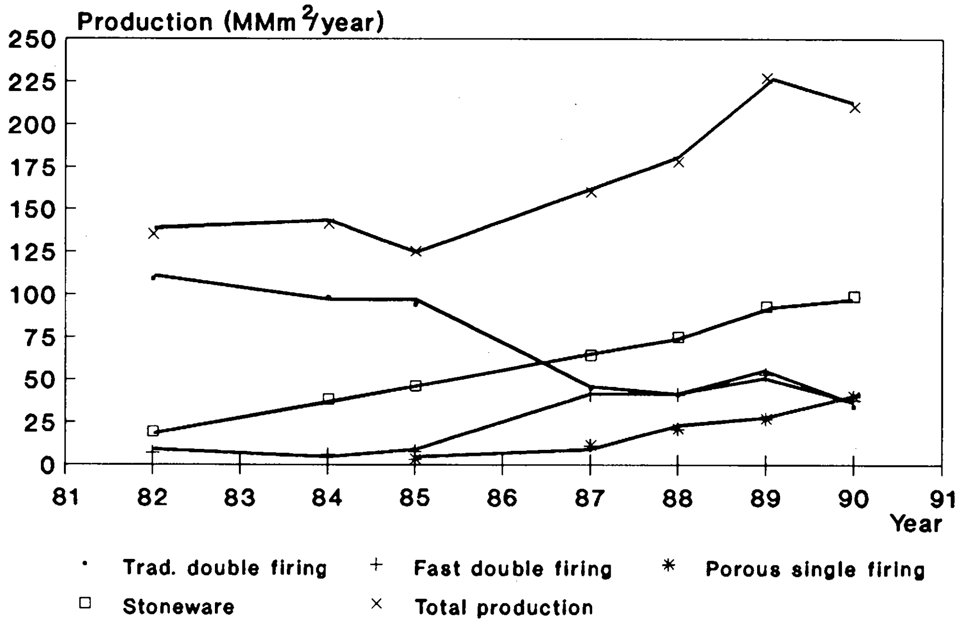
The value of the mean coefficient of expansion of the fired body is highly influenced by the quartz and carbonate content of the starting composition. Mean coefficients of expansion for single-fired wall tile bodies ranging from 70-80.10^{-7}°C^{-1} are considered recommended values.

Other defects which can arise during the firing stage are the poor dimensional stability, to be observed in fired ware with different facial sizes and thicknesses, and deformations in the finished product such as lack of rectangularity (wedging) and straightness in sides and edges. These defects are mainly due to shrinkage variations in the ware in the last part of the preheating period and during the peak temperature period. Shaping the body with suitable raw materials can reduce shrinkage to values of under 0.5%, thus virtually eliminating the possiblity of these defects appearing, in spite of the fact that the tolerance allowed for this kind of tile (group BIII), is quite limited.

7. COMPARATIVE STUDY BETWEEN THE TWO PROCEDURES USED AT PRESENT IN CERAMIC WALL TILE MANUFACTURE.

7.1 Introduction

The evolution in Spain of ceramic tile production over the last few years has been plotted in Figure 9, making use of data supplied by ASCER (Asociación Española de Fabricantes de Azulejos, Pavimentos y Baldosas Cerámicos).



Year	T.D.F.	Fast D.F.	Porous S.F.	Stoneware	T. Prod
1982	109	7		19	135
1984	98	6		38	141
1985	94	8	3	46	125
1987	45	41	11	64	160
1988	41	41	21	75	178
1989	54	53	27	93	227
1990	34	38	40	99	210

Figure 9.- Evolution of ceramic tile production in Spain.

As may be observed, in 1990, ceramic wall tile production in our country by traditional double firing, fast double firing and single firing, was virtually of the same order (34, 38 and 40 MM m /year respectively). As a clear drop in the first method may be deduced from the graphs, in the following only the last two procedures will be dealt with.

In a recent study conducted by the Centro Ceramico of Bologna (Italy), entitled "The Italian Ceramic Tile Industry and Carbon Dioxide Emissions", which has not been published, natural gas consumption required for ceramic tile manufacture by different technologies is assessed over the period 1982 to 1990. The values reported are listed in Table VIII.

Product/Technology	Natural gas consumption (Nm^3/m^2 produced)	
	1982	1990
White clay/single firing (wet method)	3.6	2.5-3.0
Red clay/single firing (wet method)	3.0-4.2	2.5-3.0
Red clay/single firing (dry method)	1.5-1.8	1.5-1.8
Double firing/second firing	2.0-2.2	1.3-1.5
Double firing/complete process	4.5-6.0	3.4-5.0

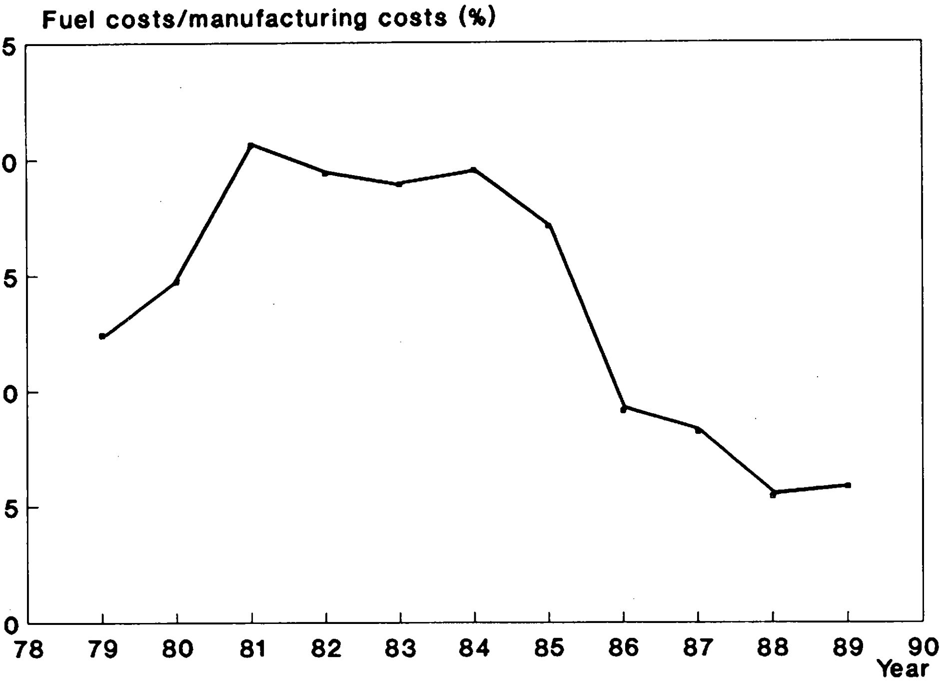
Table VIII

In this study no distinction is made regarding whether the technology indicated in the table above is applied to floor tile (stoneware body) or wall tile (porous body), and double firing is spoken of in general. However, comparing comsumption corresponding to single firing by the wet method to the lowest double-firing figures for 1990, is to the advantage of the former procedure.

At present fuel has a limited effect on total manufacturing costs, so that although indicative it cannot be considered as the sole determining factor in deciding which is the most suitable procedure. In fact, in the plot and table of Figure 10, making use of data from the above-mentioned study, the evolution of the ratio: fuel costs/manufacturing costs (in %) is reported, for 1979-1989. As may be observed, fuel costs at present represent only about 6% of total manufacturing costs. This mean value, proposed for Italy, is also practically applicable to Spain, as will be seen from figures below. As a result, when it comes to deciding what the suitable procedure is, more thoroughgoing study is required, in which not only fuel costs but also all the items contributing to total manufacturing costs, applied specifically to ceramic wall tile manufacture in Spain, are taken into account.

7.2 Cost comparison between fast double-fired and single-fired wall tile production in Spain.

The following data represent the updating of a study previously conducted by staff from the Instituto de Tecnología Cerámica [10], [11], [12], [13], [14].



Year	Fuel costs/manufacturing costs (%)
1979	12,4
1980	14,7
1981	20,6
1982	19,4
1983	18,9
1984	19,5
1985	17,1
1986	9,1
1987	8,2
1988	5,4
1989	5,8

Figure 10.- Evolution of the ratio fuel costs/manufacturing costs in Italy.

A reference production had to be set to conduct the study: 3000 m /day, as well as the choice of two formats (15x20 cm and 20x30 cm) to compare results. Moreover the following production schedule was assumed:

- The kilns and classification section worked non-stop seven days a week.

- The glaze line and press section worked 80 hours/week, in two 7.5 hour/day shifts, Monday through Friday, with one 5-hour shift on Saturday.

- Laboratories and maintenance kept a normal work day.

Other costs taken into account were:

- The average labour costs were assessed at 2.25 MM pts annually per person. All personnel was included in this average value, from the cleaner to the technical director of the plant.

- Energy costs were assessed at:

Electric energy	12 pts/kwh
Thermal energy (fuel: natural gas) (*)	
Vertical dryers	2.2 pts/th
Single-layer kilns	2.3 pts/th

- Raw materials were assessed as follows:

Raw materials for the body:

Dry-ground powder	2500 pts/tm
Spray-dried powder (5% moisture content)	4000 pts/tm

Glazes:

For fast double-firing	75 pts/kg
For porous single firing	85 pts/kg

- In the two procedures being compared, the possibility was considered of developing the process with pressing powder prepared by both the dry and wet method. In order to carry out the study on a comparative basis, in both cases, the prepared composition was purchased from a commercial supplier.

- Five years was taken as amortizing period for the facilities.

- With regard to investments, no detailed study of all the elements making up the plant was conducted, since this would only serve in the case of a specific plant. Only the most significant process units were considered, so that although analysis was simplified, the findings are comparable to those which would be obtained by a more rigorous investment study.

- As far as maintenance materials are concerned, those belonging to each section were assessed, which are normally not included in the general maintenance store, such as for example, silk screen printing screens, kiln rollers, etc.

- On computing the costs of the different options no account was taken of the losses that normally occur in each section, as these factors depend on each firm's way of working, and are therefore very variable.

- Manufacturing costs were assessed by summing labour, raw materials, electric and thermal energy and maintenance material, amortization being considered as separate costs, in order to compare separately the amount involved under this heading. The total costs were found by summing manufacturing and amortization costs.

- The following were not taken into consideration: packaging and marketing costs, costs involved in starting up the facility, investment in buildings and the price of raw materials and finished product stocks. In a more rigorous study, all these items should be taken into account in calculating total costs.

7.2.1 Single firing

The process was assumed to take place in series, without interruptions, in the pressing, drying and glazing sections, so that this group forms a productive unit.

(*) The costs for thermal energy were related to the lower heating value (LHV). Prices were applied acccording to the Official Gazette no. 273, 18/11/91.

7.2.2 Double firing

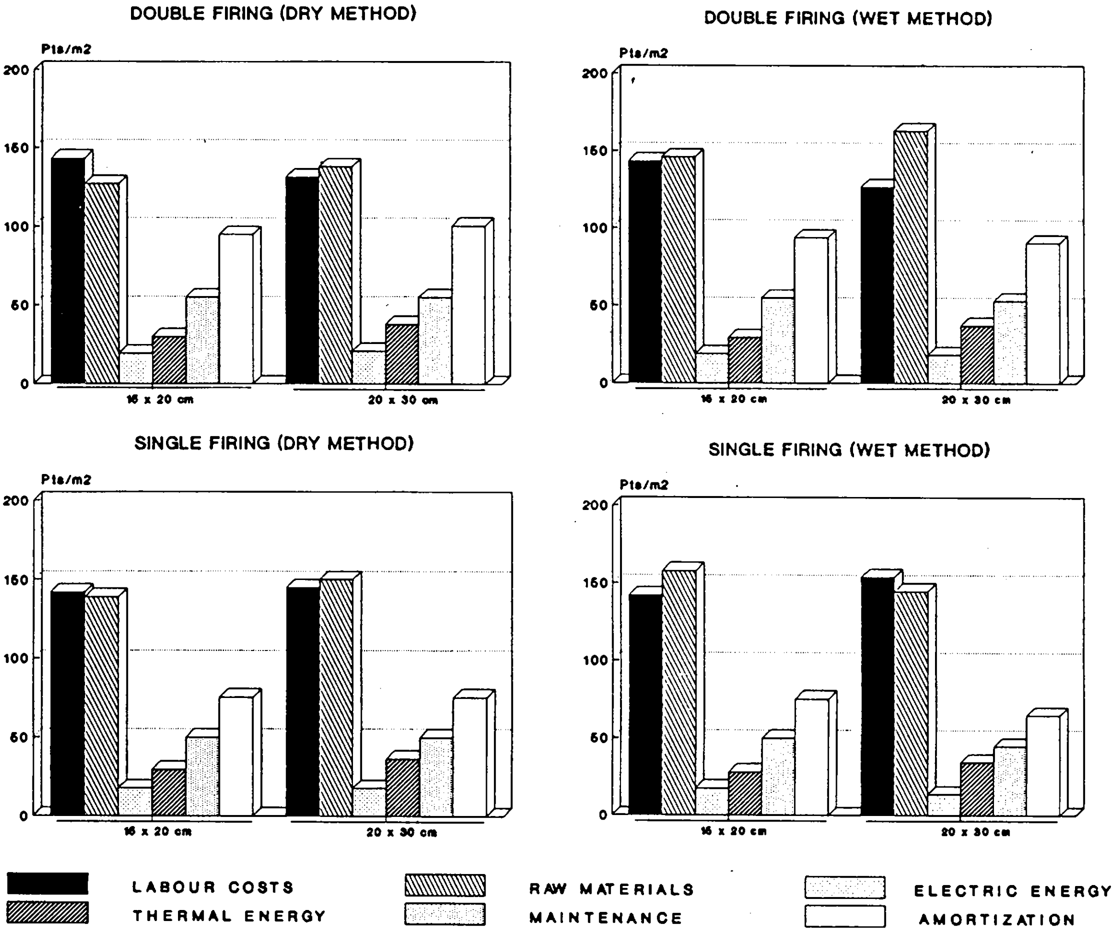
An automated plant is assumed where the ware is pressed, dried and loaded on cars, (Box-type), to be subsequently set in a single-layer kiln where first firing is conducted. The resulting biscuit is automatically classified on leaving the kiln, and is newly loaded on cars to feed the glaze line without any kind of handling, subsequently proceeding to the second firing and classification of the finished product.

7.2.3 Conclusions

The findings are reported in Table IX and Figures 11 and 12.

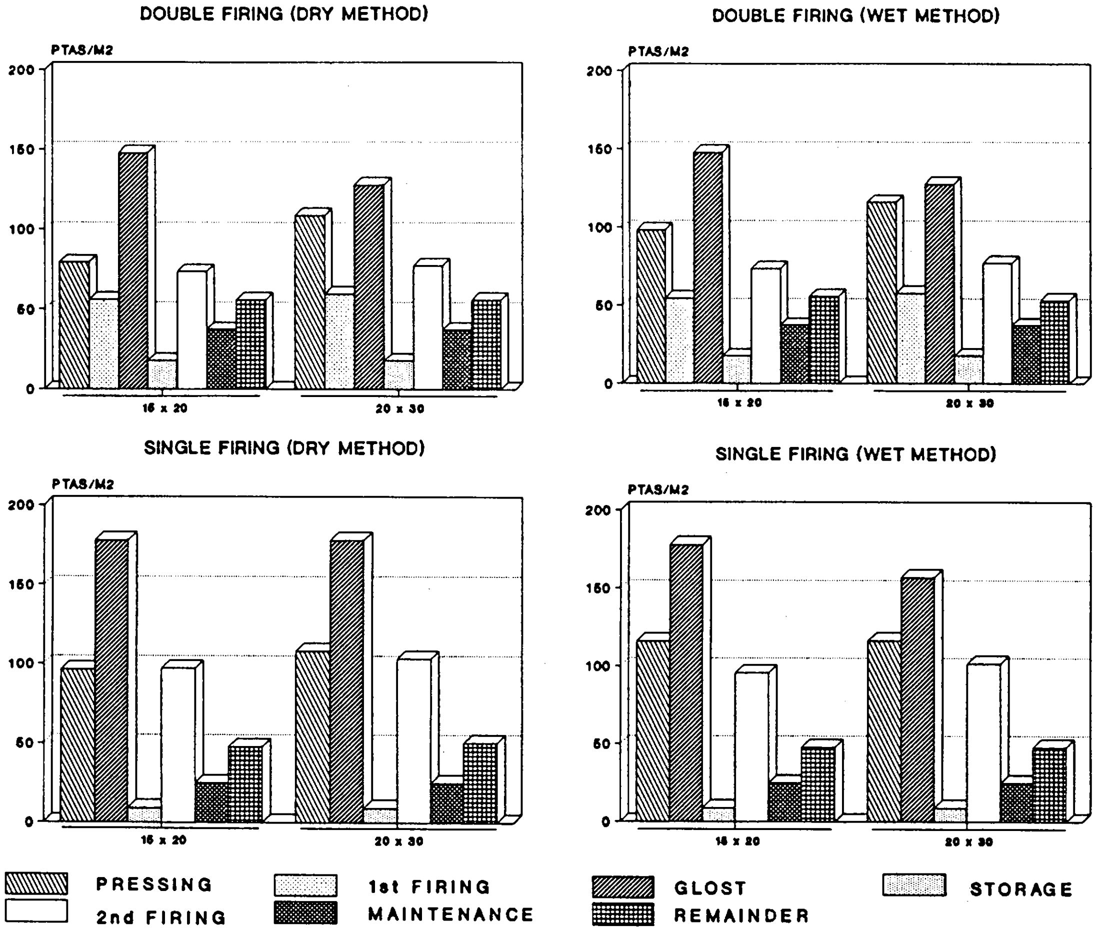
HEADING	FAST DOUBLE FIRING				SINGLE FIRING			
	DRY METHOD		WET METHOD		DRY METHOD		WET METHOD	
	15X20	20X30	15X20	20X30	15X20	20X30	15X20	20X30
Manuf. costs (Pts/m^2)	374	383	392	398	378	398	396	392
Amortization (Pts/m^2)	95	100	94	91	75	75	74	64
Total costs (Pts/m^2)	469	483	486	489	453	473	471	456
Invesment in machinery (MM pts)	519	550	514	496	413	413	408	351

Table IX



HEADING	DOUBLE FIRING				SINGLE FIRING			
	DRY METHOD		WET METHOD		DRY METHOD		WET METHOD	
	15x20	20x30	15x20	20x30	15x20	20x30	15x20	20x30
Raw materials	127	138	146	163	139	150	158	145
Labour costs	143	131	143	127	142	145	142	154
Thermal energy	19	21	19	18	18	18	18	14
Electric energy	30	38	29	37	29	36	28	34
Maintenance	55	55	55	53	50	50	50	45
Amortization	95	100	94	91	75	75	74	64
TOTAL	469	483	486	489	453	473	471	456

Figure 11.- Breakdown of manufacturing costs into headings. (pts/m).



SECTIONS	DOUBLE FIRING				SINGLE FIRING			
	DRY METHOD		WET METHOD		DRY METHOD		WET METHOD	
	15x20	20x30	15x20	20x30	15x20	20x30	15x20	20x30
Pressing	80	109	98	117	96	108	116	116
1st firing	56	60	55	58	-	-	-	-
Glost	148	128	148	128	178	178	178	157
Storage	18	18	18	18	9	9	9	9
2nd firing and classification	74	77	74	77	97	103	95	101
Maintenance	37	37	37	37	25	25	25	25
Remainder	56	54	56	54	48	50	48	48
TOTAL	469	483	486	489	453	473	471	456

Figure 12.- Breakdown of manufacturing costs into sections (pts/m).

The following conclusions were drawn on the basis of these findings, taking into account the above preestablished general conditions:

1. On analyzing the table and graph in Figure 11, where cost distribution is itemized, amortization, labour and raw materials are observed to be the headings which most affect total costs. Furthermore, it may be observed that the figure for amortization, in the case of double firing is much greater than in single firing.

2. In the table and graph of Figure 12, the pressing and glazing sections may be observed to have the greatest influence on overall costs.

3. Table IX shows that lowest total costs correspond to the single-firing process. It is to be highlighted that on calculating costs the influence of losses and classification levels were not taken into account, as the available data varied considerably per enterprise.

   As total costs for the different options are similar, the influence of these last two items could become decisive when choosing one procedure or another.

4. The single-fired procedure with powder preparation by the dry method, can reach manufacturing costs like those when operating by the wet method. However, from a technical point of view, it is preferable to use the latter method as the quality levels attained are usually higher than those reached by the former.

5. Fast double firing is seen to be an interesting option, owing to the flexibility offered by the plant, showing acceptable production costs, personnel expenditure similar to that of porous single firing and quality assurance in the manufactured product worth taking into account. However, implementation requires a considerably greater investment than for the single-firing technique (above all if one bears in mind the greater site area needed for buildings).

6. Single firing has at present reached very similar quality levels to those obtained by double firing, with analogous manufacturing costs but with lower amortization costs.

7. There has thus been a progressive implementation in Spain of the single-firing process for ceramic wall tile manufacture since 1980 (Figure 9). Moreover, this procedure, with pressing powder preparation by the wet method, can at present be considered the most viable option, both from a technical as well as an economic pont of view for the manufacture of large sizes which are in growing demand.

REFERENCES

[1] Baldosas cerámicas para revestimiento de suelos y paredes. Tomo 2.- Construcción. Recopilación de Normas UNE. AENOR. Madrid, 1988.

[2] G. Biffi. "La monocottura rapida porosa. Problemi e prospettive.". Faenza Editrize S.p.A. Faenza.

[3] Taulells; 2; 64; 1985.

[4] J.L. Amorós. "Pastas cerámicas para pavimentos de monococción. Influencia de las variables de prensado sobre las propiedades de la pieza en crudo y sobre su comportamiento durante el prensado y la cocción.". Tesis Doctoral, 1987.

[5] J.L. Amorós, F. Zaera, E. Sánchez, A. Escardino. "Estabilidad dimensional en piezas de monococción porosa.". Ponencia presentada en el II Congreso Mundial de la Calidad de Azulejo y Revestimiento Cerámico (QUALICER'92), 1992.

[6] V. Beltrán, V. Bagán, E. Sánchez, F. Negre.
"Características de las arcillas utilizadas para la fabricación de pavimentos cerámicos en pasta roja."
Técnica cerámica; 164; 280-287; 1988.

[7] E. Sánchez, J.García, V. Sanz, E. Ochandio.
"Raw material selection criteria for the production of floor and wall tiles."
Tile & Brick International; 6(4); 15-21; 1990.

[8] E. Sánchez. "Definición y características de arcillas de cocción blanca para pastas de cocción blanca."
Reunión Técnica de la Sección de Materias Primas. Jornadas Tecnicas sobre Arcillas de Cocción Blanca.
Castellón, 25-26 de Abril de 1991.

[9] J.L. Amorós, A. Blasco, J.E. Enrique, F. Negre. "Características de polvos cerámicos para prensado.". Bol. Soc. Esp. Cer. Vidr.; 26(1); 31-37; 1987.

[10] A. Blasco, J.L. Amorós, M. Sancho-Tello, V. Beltrán. "Estudio de los costes de producción y de la inversión en plantas de pavimento de gres de monococción por vía seca y por vía húmeda. 1ª parte." Técnica Cerámica; 116; 1208-1225; 1983.

[11] A. Blasco, J.L. Amorós, M. Sancho-Tello, V. Beltrán. "Estudio de los costes de producción y de la inversión en plantas de pavimento de gres de monococción por vía seca y por vía húmeda. 2ª parte." Técnica Cerámica; 117; 1266-1274; 1983.

[12] J.C. Jarque, J. Lezaun, J.M. López, G. Mallol, E. Monfort. "Viabilidad técnica y económica de los procesos productivos actuales de fabricación de azulejos.". Técnica Cerámica; 189; 714-722; 1990.

[13] A. Blasco, G. Mallol, J.C. Jarque, E. Monfort. "Estudio de los costes de fabricación y de la inversión en plantas de producción de gres porcelánico. I." Técnica Cerámica; 193; 328-340; 1991.

[14] A. Blasco, G. Mallol, J.C. Jarque, E. Monfort. "Estudio de los costes de fabricación y de la inversión en plantas de producción de gres porcelánico. II." Técnica Cerámica; 194; 386-400; 1991.