

RAW MATERIAL SELECTION CRITERIA FOR THE MANUFACTURING OF CERAMIC PAVING AND TILING

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1.- INTRODUCTION

A wide variety of ceramic products are currently manufactured in Spain for use in cladding of walls and floors, with different characteristics and manufactured using different production systems.

The manufacturing of ceramic paving and tiling is of great interest in the Community of Valencia, as Spain is the third-ranking producer in the world, with some 200 - 220 million m²/year, this production being greatly concentrated in the Community of Valencia. Of some 220 companies in Spain, some 180 are located in the Community of Valencia.

It is also an eminently exporting sector, with exports of some 65 - 70 million m² per year (some 40% of production), European Community countries being the main destination.

For the manufacturing process, the starting point is a series of raw materials which undergo transformation in order to achieve the desired properties of the finished product.

Product quality is related to the composition of raw materials used and the procedure followed during manufacturing.

In the manufacturing of ceramic paving and tiling the composition has to be adapted in each case in function of the characteristics of the ceramic piece which it is wished to obtain, as does the manufacturing process (1).

The compositions used have followed an evolution over time linked to the technological changes undergone in the manufacturing process, adapting to rapid firing cycles and manufacturing of the glaze and the "single firing" base by simultaneous firing. Higher market requirements with respect to the quality of ceramic materials have also led to the use of raw materials of greater quality and with a higher degree of refinement (2).

2.- SELECTION CRITERIA

Ceramic products used for cladding walls and floors can be divided according to diverse classification criteria, in function of their appearance, the use to which they are to be put, characteristics of the manufacturing process and properties of the finished product.

2.1.- CLASSIFICATION

These classification criteria are not exclusive, each particular case being included under the different types of classification used:

2.1.1.-Coloration of the body

Manufactured ceramic paving and tiling products can be divided, in general, into two broad groups:

- White body products.
- Buff body products.

Not only by the characteristics of the finished product, in which the fundamental difference is the colour of the body, but also by the type of composition used, especially in the Community of Valencia, where red clays are almost exclusively used in the manufacture of buff body products, while a mixture of clay and degreasing raw materials which normally require a higher degree of grinding is used for white body products.

Under a separate heading are the compositions used for the manufacturing of rustic products which use clays of characteristics rather closer to white firing clays, though with higher iron content, to which are usually added inert degreasing agents in order to reduce contraction.

Owing to the availability in Spain of natural red clays (with high content in iron oxides) of suitable characteristics, production is heavily orientated towards the manufacturing of "red p te" tiles, with current production of "white body" ceramic tiles being lower than 10% of total production.

2.1.2.- Use to which they will be put

Ceramic tiles are mostly used for:

- Tiling of walls.
- Paving of floors.

Spanish manufactures of ceramic tiles have been traditionally orientated towards production of tiles for wall tiling. With the introduction of the single firing system at the beginning of the 'eighties, the production of tiles for paving increased, reaching in 1984 just over 30% and at present around 50% of production.

2.1.3.- Characteristics of the manufacturing process

Looking at the various phases of the manufacturing process, the following divisions can be made:

a) GRINDING

- Humid process.
- Dry process.

The traditional dry process grinding with natural humidification has evolved towards granulation in the dry processes with large-scale introduction of humid process grinding, especially when quality requirements are high. At present in Spain humid process grinding is used in a proportion greater than 70%.

b) PIECE FORMATION

- Pressing.
- Extrusion.

Pressing is the manufacturing process most used for the manufacture of ceramic tiles, due to the greater dimensional stability achieved with this moulding process. In Spain the manufacturing of tiles by pressing is around 95%, although in recent years there is rather more manufacturing of rustic vitreous tiles by extrusion.

c) FIRING

In the firing phase, two different classifications may be made, in function of the duration of the firing cycle:

- rapid.
- slow.

and of whether or not the firing of the base is carried out simultaneously with that of the glaze:

- single firing
- double firing

The evolution of this phase has been directed towards maximum reduction of the cycles (increase of productivity) and the carrying out of a single firing. In the manufacturing of paving products, these technologies have been more quickly and easily assimilated.

2.1.4.- Properties of the finished product.

The classification proposed in European norm EN-87 for ceramic tiles is made in function of their water absorption capacity, whether they are glazed or not and the piece-formation procedure, on the basis of which it defines some characteristics they should comply with. The groups of products most usually manufactured are the following:

- Pressed glazed ceramic tiles of high water absorption (> 10%). B III GL. ("tiles").
- Pressed glazed ceramic tiles of medium water absorption. B II a GL.
- Pressed unglazed ceramic tiles of low water absorption, B I UGL. Porcelain vitreous ceramics is not included in this group.
- Unglazed extruded rustic vitreous tiles included within the groups of extruded ceramic unglazed tiles of medium and low absorption. AIUGL and AIIaUGL.
- Some other less widespread products.
- Unglazed pressed products of high water absorption. B III UGL.
- Unglazed pressed products of medium water absorption. B II UGL.
- Extruded glazed products of low water absorption. AI GL.

2.2.- CHARACTERISTICS OF THE COMPOSITIONS

For the manufacture of a particular ceramic tile, the composition must comply with the requirements, and shall impose each of the chosen options of the various classification criteria.

2.2.1.- Coloration of the body

The division which arises in function of firing colour shall delimit the colourant oxide content (principally of iron oxides) of available raw materials. The whiteness of the fired pieces is in function

of that iron oxide content, although the form in which that element is present in the raw materials is of great importance: integrated into the clayey structure, in the form of different iron compounds, as soluble iron salts or in the form of the metal iron.

It also depends upon the presence of other colorant oxides, such as titanium oxide which gives a yellowish colour, on the type and quantity of glass phase formed in the fired piece, which may mean that a greater or lesser proportion of iron goes to form part of the latter, and on the facility of formation of crystalline phases which may occlude the iron oxide in their structure. The most usual crystalline phases developed are the formation of mullite on the basis of the kaolinitic clayey minerals and the formation of calcic silicon aluminates (anorthite) on the basis of the clayey minerals and the calcium oxides.

As a very general classification, we may consider that clays with iron content lower than 2% can be used in white-body products, and the degreasants with a content lower than 0.5%.

2.2.2.- Uses of the product

In general, the compositions used for paving and tiling present special characteristics in function of the properties required for each use, and in a certain sense some peculiarities in their placing.

a) WALL TILING

High dimensional stability is generally required of tiling products, this being obtained by use of a composition with a low firing contraction. This low firing contraction is linked to high porosity, which also means greater ease of placing.

The porous piece is also very accessible to water, hydrating the amorphous and vitreous phases present, which brings with it an increase in size of the fired piece and may lead to curvature or crazing of the glaze. Owing to this the fired pieces must present a high proportion of crystalline phases with minimum presence of amorphous phases.

Dimensional stability, high porosity and stability of the phases present is normally achieved by introduction of calcium and magnesium carbonates into the composition. The calcium and magnesium carbonates react with the amorphous phases resulting from dehydration of the clayey mineral to form calcic and magnesian silicon aluminates stable to the action of humidity.

For tiling compositions, clays and other raw materials will have to be introduced to provide alkaline earth oxides. Clays with a proportion of calcium carbonate greater than 5% are considered typical of wall tiles.

b) PAVING

The paving product is normally characterized by high mechanical strength of the fired pieces, and in some cases good performance under conditions of freezing. This is normally achieved with reduction of the porosity of the pieces as a consequence of formation of the vitreous phase. This fusing effect is usually achieved by introduction of raw materials which provide alkaline oxides.

This reduction of porosity is normally accompanied by a high firing contraction, which will be greater the lower the porosity of the piece.

Raw materials for paving have to provide alkaline oxides to a greater or lesser extent, in function of firing temperature. The supply of alkali earth oxides normally reduces the firing range and increases deformations, so that clays with calcium carbonate content higher than 5% are not considered to be suitable for paving.

2.2.3.- Characteristics of the manufacturing process.

a) GRINDING

The size-reduction operation is carried out by increasing the reactivity between the materials and reducing the incidence of impurities present. A subsequent sieving operation is associated with this operation in order to separate particles of larger size.

A first aspect to be considered in raw materials, related with grinding, is their hardness, or difficulty in disintegration. Some raw materials, such as pegamatites, talcs, dolomites, and even some compact clays such as those from Moró, are not very suitable for dry processing due to the high abrasion of the mills, with an increase in the quantity of impurities and difficulty in obtaining fine granulometries in the usual industrial installations for composition preparation.

Humid process grinding also allows a better sieving to be carried out in order to eliminate the impurities present in raw materials. This means that clays with impurities which are difficult to grind, such as chalks, dolomites, pyrites, carbon, etc., are more problematical to use in dry processes.

Another aspect to be considered is difficulty in deflocculation of the composition, either because any of the clays present has excessive plasticity or due to the presence of soluble flocculant salts, normally sulphates. This makes the clay suitable or otherwise for humid processing, unless it is used in very small proportions. The use of compositions difficult to deflocculate would mean additional cost due to the increased quantity of deflocculants to be used, or due to the low solids contents used in the grinding and atomization.

A possible limit of the soluble sulphate content in clays for use in humid process grinding is 0.2%.

b) PIECE FORMATION

As regards the moulding process used in formation of the piece, on occasion the compositions used present some differences.

In extrusion processes greater plasticity is needed than in pressing for good functioning of the extruding machine. This high plasticity has to be linked to low drying contraction and a high permeability which facilitates drying and degasification during firing. This is achieved by using compositions with a high proportion of plastic clayey material and with inert degreasing agents of thick granulometry, normally shamottes of refractory clays.

c) FIRING

As has been mentioned above, firing of the body and the glaze can be carried out simultaneously or consecutively, which will lead to the processes of single firing or double firing, respectively.

In single firing processes there may exist interference between the degasifications undergone by the piece in the course of firing and the glaze during its fusion, so that it is best to use compositions with a lower proportion of compounds which undergo decomposition, especially if at high temperature and if their particle size is high.

In single firing compositions with a rather lower proportion of carbonates are normally used than in double firing, and some impurities such as sulphates or carbon are more problematical, for they decompose at high temperature.

The maximum permissible quantity of sulphates in single firing processes may be located at 0.2% in weight of SO_4 .

Inorganic material content is also a more limiting factor in single firing processes, since the accessibility of the oxygen necessary to oxidize it is reduced when the glaze makes the piece impermeable. The maximum permissible quantity of inorganic material in the rapid single firing process is estimated at 0.3%, measured as total carbon.

As regards the duration of the firing cycle, two aspects may be considered:

- The organic material in the composition has to be oxidized in the course of firing. In rapid firing processes, this oxidation reaction occasionally limits the maximum possible velocity of the firing cycle. It can be estimated that in firing processes it is not advisable to use compositions with inorganic matter content higher than 0.4%.
- The granulometry of the raw materials which take part in the rapid firing processes has to be finer so that they complete the various reactions, especially that of some impurities such as the thick "caliche" calcite particles which need a longer time to react with the clayey minerals or decompose totally. Owing to this, clays with impurities are not advisable for rapid firing processes, especially if they are to be dry processed.

3. PRODUCTIVE OUTLINES

Within the various types of ceramic tiles existing on the market, we may consider as most significant, in view of the different properties of the final product, the following:

- Porous tiles
- Vitrified paving
- Vitreous porcelain
- Unglazed rustic vitreous ceramics

Logically, not all the manufacturing processes are used to produce the various products existing, for the different properties of the final product make it advisable to manufacture them one way or another. We provide details below of the different manufacturing sequences followed in each case.

3.1.- POROUS TILES Figure 1 shows in diagrammatic form the most usual procedures for manufacturing of porous products for wall tiling.

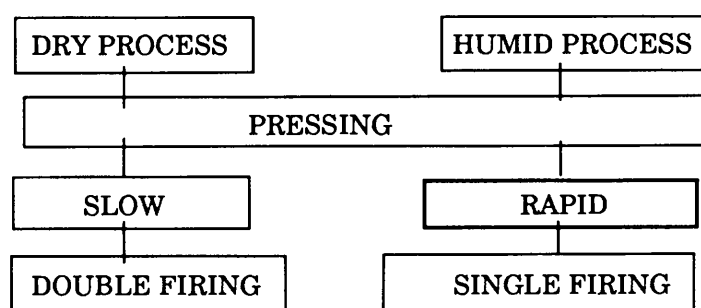


Figure 1. Porous tiles

The piece-formation procedure exclusively used is that of pressing, due to the high dimensional stability required of wall tiling products. When dry process grinding is used, firing of the body and the glaze is generally carried out independently, due to the problematic loading of the presses and the delay in degasification of the larger-size impurities obtained by dry process. If slow firing of the body is used, with piled pieces, the glaze is submitted to a second firing, which can be slow or rapid.

3.2.- VITRIFIED PAVING

In this type of products the grinding is mostly carried out by humid process, for the granulated raw material obtained is more suitable for correctly carrying out loading of the presses. Extrusion is little used due to the dimensional stability problems it presents, and when it is used it is linked to a dry process grinding, which is accompanied by glazes of more rustic finish. Simultaneous firing of the glaze and the body is used in all cases, due to the problems of glazing a low-porosity fired piece.

Figure 2 sums up the most commonly used manufacturing steps.

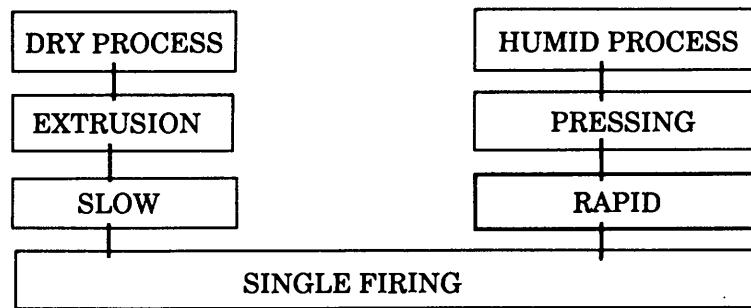


Figure 1. Vitrified paving.

3.3.- PORCELANIC VITREOUS TILES

The manufacturing process exclusively used is that corresponding to figure 3.

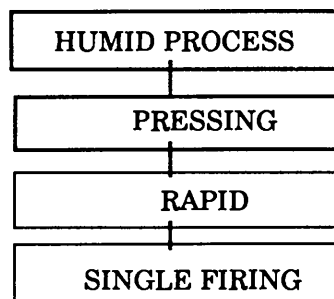


Figure 3. Vitreous porcelain.

The grinding in this process is always humid process, owing to the fine granulometry and rigorous screening required to achieve the desired characteristics. The piece-formation procedure used is that of pressing, owing to the greater dimensional stability it provides. The product is not glazed, being decorated during the pressing operation by combining granules of different colour in the body.

3.4.- UNGLAZED RUSTIC VITREOUS CERAMICS

Dry process grinding is normally used due to the rustic appearance of the compositions and the need for addition of schamottes (saggar clays) of thick granulometry. Extrusion is the procedure mostly used for piece formation due to the more rustic appearance of the pieces, which do not normally require high dimensional stability, and to the low surface porosity of the moulded pieces. The tiles are not generally glazed, and where they are glazed they are manufactured by single firing.

The most usual factory chart is summarized in figure 4.

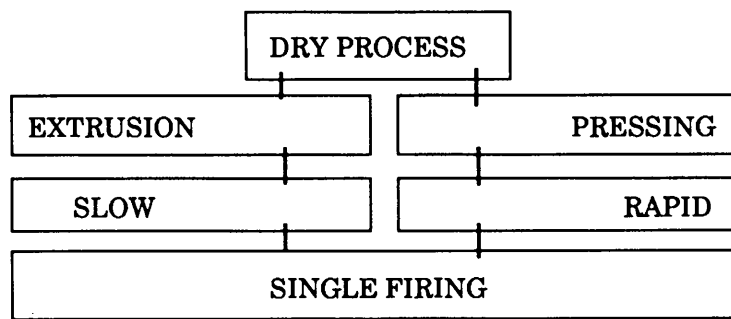


Figure 4. Unglazed rustic vitreous ceramics.

4.- COMPOSITIONS USED

In accordance with the characteristics of the finished product and of the different manufacturing steps normally used, the most suitable raw materials for the formulation of the composition have to be chosen.

4.1.- POROUS WALL TILES

As we saw above, compositions with a high proportion of calcium carbonate (=15%) are used in the manufacture of porous wall tiling products, in order to achieve porous products with hardly any firing contraction and stable to humidity.

Figure 5 shows the firing range for this type of composition. It can be seen that in the working zone (1080-1110°C) firing temperature variations have little effect on the size of the pieces (a 10°C firing temperature difference results in 0.05 - 0.10% variation in firing contraction). Normally, the higher the calcium carbonate content and the more refractory the minerals present in the composition, the lower is the variation of lineal contraction and of water absorption with firing temperature (4).

This low firing contraction is also achieved by adding calcium carbonate and inert degreasing agents which improve compaction of the pieces and reduce firing contraction. The low firing contraction means that differences of compaction due to variation in the pressure or humidity of the pressing have little effect on the size of pieces. In these compositions a variation of apparent density of 0.050 g/cm³, equivalent to a variation of press pressure of 50 kg/cm² (5), results in a firing contraction variation of 0.1%.

Finally, the composition must present an adequate proportion of fusible clayey minerals to provide the glass phase necessary to obtain mechanical resistance under firing suitable to the working temperature.

The compositions used for the manufacturing of porous wall tiles are totally different in function of the colour of the body, being divided into compositions of buff body and white body.

4.1.1.- Buff body porous wall tiles

Normally used for these compositions is a mixture of natural clays of high iron content, varied plasticity and variable quartz and calcium carbonate content, until the desired properties are achieved (6) (7) and (8).

The raw materials used are as follows:

Clay	Carbonate content	Quartz	Plasticity
Araya	+++	+	+
Sichar	++	++	++
Mas Vell	++	+++	++
Bugarra	++	-	+++
Chulilla	+	+	+
Geldo	+	-	+++
Useras	+	+	+
Galve	-	++	++
Villar	-	++	++
Moró	-	+++	-

Recourse is occasionally had to addition of small proportions of sands, wadding and shards in order to reduce firing contraction.

4.1.2.- White body porous wall tiles

For these porous wall tile compositions a mixture of clays of differing plasticity and low iron content is used together with a series of degreasing agents to reduce contraction and to supply alkali earth oxides. This type of composition generally requires a high degree of whiteness, so that various proportions of kaolin are occasionally added.

The following raw materials are normally used:

Clays	Whiteness	Plasticity	Fusibility	Quartz
Imported clays	++	+++	+++	++
Domestic clays	+	++	++	+++
Kaolins	+++	++	+	+

Degreasing agents (calcite, dolomite, sands, talcs, etc.)

4.2.- VITREOUS PAVING

As we indicated above, vitreous paving compositions are of low porosity.

Easily vitrified compositions with adequate formation of the glass phase at the desired firing temperature are needed. The glass phase should not present an excessively low viscosity which might lead to firing deformations.

In buff body compositions alkaline fluxes of the illitic clays are used, while Na and K feldspar are used in white buff compositions. The presence of calcium oxides is not advisable, as they enter the glass phase markedly and rapidly reduce its viscosity, making plugs and deformations appear more easily.

Normally the higher the fusion of the composition the greater the variation of firing contraction and water absorption with temperature in the normal working zone, making plugs due to temperature differences more problematical.

Figure 6 shows the firing range of these compositions. It can be seen that in the working zone (water absorption = 0.4%) a 10°C variation in the working temperature leads to a firing contraction variation of 0.35 to 0.45% (9).

In order to obtain this low water absorption it is necessary that the piece contracts. This high firing contraction is the main problem in manufacturing, for compaction variations have a marked

effect on piece size. In these compositions a variation of the dry bulk specific density of 0.05 g/cm³, equivalent to a 2% variation, affects firing contraction by 0.4-0.5%, that is, some 4 to 5 times more than in porous wall tile compositions.

Compositions therefore have to be formulated which present low porosity in the raw, with granulometric distribution suitable for packaging and low loss by roasting: firing contraction is minimized in order to achieve the low porosity desired.

Vitrified paving compositions are also totally different in function of whether the products are of red or white buff.

4.2.1.- Red buff vitrified paving

In the compositions utilized for the manufacturing of red buff vitrified paving a mixture of natural red clays of varying quartz content and with hardly any carbonates is used in order to achieve the maximum degree of compaction together with suitable plasticity.

The following red clays are used:

Clay	Plasticity	Quartz content
Plastic Villar	+++	+
Sandy Villar	++	+++
Galve	++	++
Moró	-	+++

4.2.2.- White buff vitrified paving

These compositions take as a base clayey minerals similar to the body of wall tile compositions; the whiteness requirements are not so important, while the degree of compaction achieved is important, so kaolins are not normally put into the composition. This collection of clayey minerals is linked to a series of fluxing degreasers which at the same time reduce the firing contraction necessary to achieve the desired water absorption.

A summary is provided below of some characteristics of the raw materials used:

Clays	Origin	Whiteness	Plasticity	Flux
Importation	U.K.	+++	+++	++
	France	+++	Variable	+
	Germany	+++	+++	++
Domestic	Teruel	+	+	+
	Asturias	+	++	++

Degreasing agents (feldspar, quartz, talc, etc.)

4.3.- PORCELANIC VITREOUS TILES

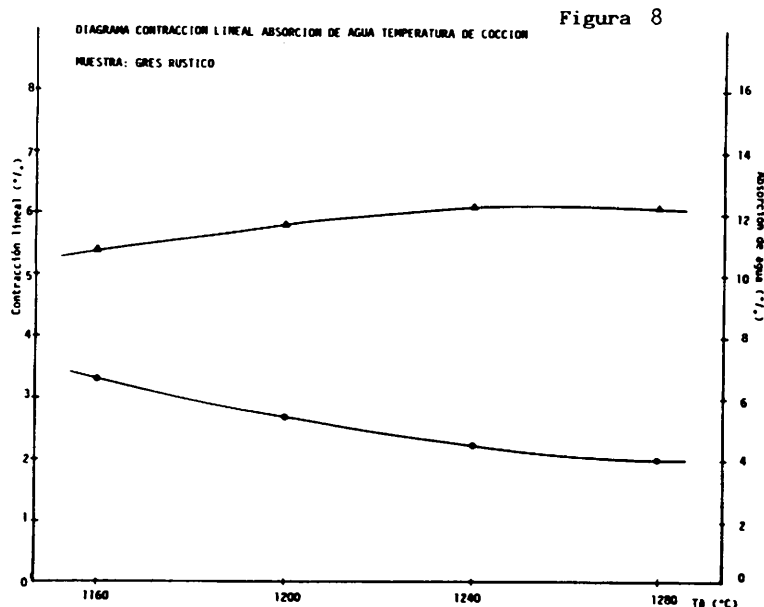
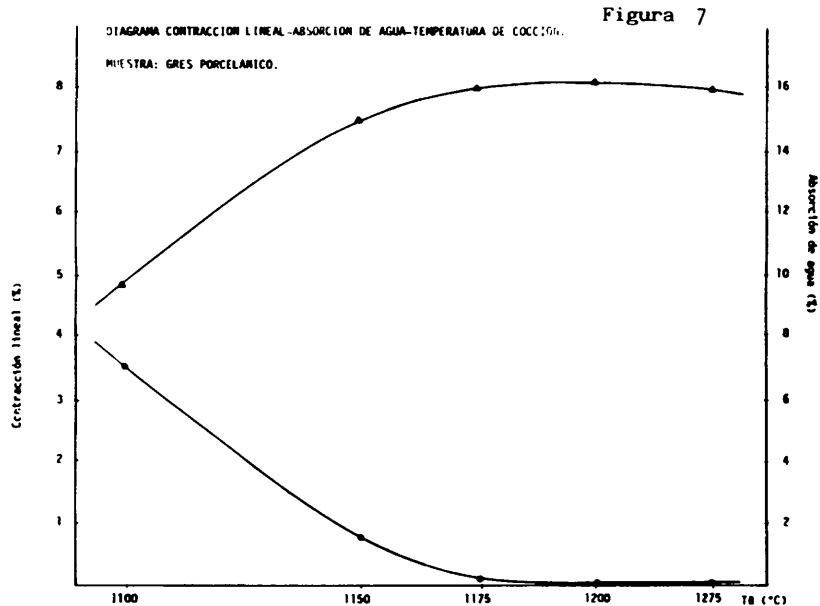
The compositions of porcelanic vitreous tiles are typical ones, similar to those of vitrified paving with low water absorption, though with some special features. Open porosity has to be very low (normally lower than 0.05%), and even closed porosity cannot be very high. This is due to it being a product which is manufactured unglazed and for use as floor tiling, so that it must have at least partial

resistance to staining. The composition therefore needs to achieve a high degree of vitrification, which goes with high firing contraction.

In order to close the majority of the pores, a very fine porosity has to be taken as a starting point, allowing the pores to be easily sealed with the glass phase formed; there must be no impurities in manufacturing which might give rise to degassing at high firing temperatures and increased internal porosity.

In order to obtain these small pore sizes, very fine granulometries have to be used in the composition; these are normally unsuitable for packing, while high raw porosity is obtained which is linked to the high reduction of porosity and involves high firing contractions. The combination of raw materials most suitable for obtaining a maximum degree of compaction in spite of their fine granulometry has therefore to be used, thus reducing firing contraction.

Figure 7 shows the firing range of a typical porcelanic vitreous tile. It can be seen that in order to achieve the desired porosity the firing contractions are very high (8%) (in spite of the pressing pressures used being very much greater than those of conventional vitreous ceramics), and that in the working zone temperature variations have hardly any effect on the size of the pieces.



Owing to this high firing contraction, variations of porosity in the raw do on the other hand have a great effect on piece size, so that a variation of bulk density of 0.05 g/cm³ leads to a variation of firing contraction of 0.07-0.09%, almost double that of a vitrified paving tile.

Also of great importance is the whiteness of the fired pieces, for as they are not glazed products and are coloured en masse, the development of colour is related to the degree of whiteness achieved. Raw materials would thus have to be used with a much lower content of iron and other colorants than in the case of other uses, and they have to be similarly free from impurities which might increase the internal porosity of the fired pieces.

As we have indicated, the compositions are similar to those of vitrified paving tiles, differing only in the degree of whiteness of the raw materials used and in the lower proportion of random impurities, avoiding the use of domestic clays owing to their higher iron content.

The raw materials used are thus:

Imported clays (France, Germany, United Kingdom).

Degreasing agents (feldespars, quartz).

4.4.- RUSTIC VITREOUS TILES

In compositions for unglazed rustic vitreous tiles, normally manufactured by extrusion, a mixture of clays of different flux and iron and titanium oxides is used, providing pleasant colours on firing at low porosity. Saggar clays of thick granulometry are normally added to facilitate drying and firing and to reduce contraction.

The adding of a saggar clay of thick granulometry provides a gentle variation of the firing contraction and of water absorption with the firing temperature, owing to the good level of compaction reached during extrusion and the thickness of the pore size.

Figure 8 shows a firing range for an extruded rustic paving tile. It can be seen that a 10°C variation in firing temperature has very little effect on piece size (0.05-0.10 % C.L.), although it does normally affect the firing colour. It is more difficult to reduce the water absorption value when the schamotte granulometry used is thicker, although drying and firing are facilitated.

The main problem in manufacturing is that of dimensional stability of the pieces, owing to irregularities in the extrusion and cutting of the pieces and variations in the mulling water which affect the various values of drying contraction. A 1% variation of the mulling water shows itself in a 0.4-0.5% variation of the drying contraction.

The raw materials normally used for the manufacturing of unglazed rustic vitreous ceramic tiles are as follows:

Clays	Plasticity	Flux	Quartz
Alcañiz	+++	+	+
Estercuel	+	++	+++
Villar	++	+++	++

Degreasing agents (schamotte of fire clay)

Figure 9 indicates by way of summary, for the four types of product studied, the major sets of problems involved in manufacture thereof and their most representative characteristics.

5.- RAW MATERIAL AND COMPOSITION SELECTION CRITERIA

As we saw above, raw materials must be selected in function of the properties of the product to be manufactured and in function of the characteristics of the manufacturing process, with attention naturally being given to other criteria such as availability, homogeneity, certainty of supplies, price, etc. A selection system is proposed below, with considerations on suitability of raw materials for specific uses.

These selection criteria are of course also defined for us by the main properties to be controlled in each of the raw materials used in the manufacture of the various types of products. The procedures used for carrying out the different controls are described in detail in the bibliography (10).

We shall divide the selection system into two broad groups - clayey materials and degreasing agents - as the first are chosen mainly in function of the characteristics of the manufacturing process, while the second are characteristics of the various products manufactured, with selection and the controls to be carried out being in function of the role they play in the composition.

5.1.- CLAYEY MINERALS

Functions:

- Plastic material. As plastic raw material acts as suspension agent, it facilitates moulding of the piece and provides the mechanical strength necessary for its manipulation.
- Supply of oxides. As a clayey material it provides silicon and alumina oxides, which occasionally go to form part of the glass phase, or form crystalline phases either by themselves (mullite) or by reaction with other oxides (anorthite).

Selection criteria:

In function of each of the following controls to be carried out, a clay will be suitable for the manufacture of some types of product and using a given production system.

a) Determination of iron content and/or firing colour:

- Porcelanic vitreous ceramics.
- White body.
- Buff body.
- Rustic vitreous.

b) Determination of carbonate content.

- Vitrified paving.
- Porous cladding.
- Unsuitable owing to excessive proportion of carbonates.

c) Determination of impurities present.

c.1.- Organic matter. Black core trial.

- Rapid cycle.
- Slow cycle.
- Unsuitable owing to excessive proportion of inorganic matter.

c.2.- Other impurities (sulphates, carbon, pyrites, etc.)

- Rapid cycle - humid process.
- Rapid cycle - dry process.
- Slow cycle.
- Not useful owing to excessive proportion of impurities.

d) Determination of the deflocculation curve.

- Wet process.
- Dry process.

e) Determination of the degree of compaction under certain preparation conditions (bulk density dry).

- Vitrified paving.
- Porous cladding.
- Unsuitable owing to very poor compaction.

f) Determination of plasticity and/or mechanical resistance dry.

- Extrusion.
- Pressing.
- Unsuitable due to excessive plasticity.
- Suitable in small proportion.

g) Determination of firing contraction and water absorption at different firing temperatures.

- Low firing temperature
- High firing temperature
- Unsuitable due to excessive refraction or melting.

h) Expansion curve.

- Suitable
- Unsuitable due to high or low expansion or because of excessive proportions of free quartz.

i) Bigot curve. Water from the compo contraction of the dry residue.

- Extrusion
- Pressing
- Unsuitable due to excessive contraction of the dry residue or due to difficulties with same.

j) Chemical, mineralogical and granulametric analysis to confirm the above mentioned physical tests.

	MANUFACTURING PROBLEM			FINISHED PRODUCT PROPERTIES	
	TEMPERATURE INFLUENCE	CONFORMATION CONDITIONS INFLUENCE	DIMENSIONAL STABILITY ACHIEVED	MECHANICAL STRENGTH	SPECIAL FEATURE REQUIRED
POROUS WALL TILING (BIII GL)	LOW CONTRACTIONS OF DRYING AND FIRING	LOW	LOW	HIGH	MEDIUM-LOW RESISTANCE TO CRAZING
VITRIFIED PAVING TILES (BI GL AND BIIa GL)	HIGH FIRING CONTRACTION	HIGH	MEDIUM	MEDIUM	---
RUSTIC VITRIFIED TILES (AInGL and AIIa nGL)	HIGH FIRING CONTRACTION	LOW	MEDIUM	MEDIUM	LOW RESISTANCE TO CHEMICAL ATTACK
PORCELANIC VITREOUS TILES (BI n GL)	VERY HIGH FIRING CONTRACTION	LOW	HIGH	HIGH	LOW RESISTANCE TO STAINS

FIGURE 9. Table summarizing characteristics .

5.2.- DEGREASING AGENTS

5.2.1.- Feldspars

Functions:

- Degreasing. Increase permeability by facilitating drying and firing degassing. Improve compaction in raw, reducing firing contraction.
- Flux. Forms glass phase, reducing firing temperature necessary to achieve porosity.

Controls:

- Granulometric distribution. All the properties mentioned above, in function of its granulometry.
- Fusion cones. These indicate the degree of melting and some impurities present.
- Chemical and mineralogical analyses. Where necessary to complete the foregoing information.

5.2.2.- Siliceous and feldspartic sands

Functions:

- Degreasing. As in the case of feldspars, they increase permeability and improve compaction. They facilitate deflocculation, but in excess they reduce mechanical resistance in dry and under firing.
- Increase the expansion coefficient. In paving and wall tile body, usually only a small proportion enter the glass phase, remaining as quartz of high expansion coefficient.

Controls:

- Granulometric distribution.
- Loss by roasting. In order to detect the presence of clayey minerals.
- Control of carbonates.
- Fusion cone. At high temperature (1350°C), in order to evaluate colour, fusion and impurities.
- Chemical analysis, in order to complete the information and detect the proportion of feldspars present.

5.2.3.- Calcium carbonates and dolomites

Functions:

- Degreasing. Normally of fine granulometry, which does not improve compaction in raw, though it does reduce the plasticity of the composition.
- Supply of CaO and MgO. To react with the clayey minerals and form stable crystalline phases of higher expansion coefficient.

Controls:

- Granulometric distribution. Related with the properties mentioned above and with the temperature necessary to complete degassing of the carbonates.
- Loss by roasting. This gives an approximate indication of the purity of the carbonate.
- Thermogravimetric analysis. To determine the purity and the temperature at which

degassings are completed, detecting the presence of some impurities such as sulphates.

- Firing colour.
- Total chemical analysis and analysis for soluble salts. With the object of completing the above information.

5.2.4.- Talc

Functions:

- Degreasing. Although normally added in small proportions, its effect on the properties of the raw piece is limited.
- Fusing agent. With alkaline oxides normally forms fusion eutectics which reduce the firing temperature necessary to achieve the desired porosity or increase the mechanical strength in firing.

Controls:

- Granulometric distribution. - Carbonate content. Occasionally tends to present dolomite impurities. - Firing colour. To detect the presence of some impurities.
- Chemical analysis. To complete information and determine the proportions of chlorite and talc.

5.2.5.- Schamottes

Functions:

- Degreasing agent. Of very thick particle size in order to facilitate drying and degassings and reduce drying and firing contraction.
- Inert. Owing to its coloration and large particle size it produces effects on the surface of the finished piece.

Controls:

- Granulometric determination. Complete definition of its behaviour in the manufacturing process.
- Determination of impurities. Owing to its very large particle size the impurities it may present are not eliminated. One form of control can be high-temperature roasting and detection of the free calcium oxide with phenolphthalein.

6.- CONCLUSIONS

In accordance with the points mentioned above, there are different types of ceramic products used for paving and wall tiling, of different characteristics and manufactured by different procedures.

Compositions have to be adapted not only to the characteristics of the finished product, but also to the various manufacturing processes, with composition and clayey mineral selection criteria and manufacturing controls being adapted to each specific case.

The use of degreasing agents is normally in function of the characteristic of the product to be manufactured, and the controls to be carried out are related with the function which each raw material exercises within the composition.

7.- BIBLIOGRAPHY

- (1) Schuller, K.H.; Hennicke, H.W., "On the systematics of ceramic materials", Ber. DKG; no. 61 7, 259-263 (1985).
- (2) Kuhnelt, R.A., "Quality Assurance of Raw Materials", Intercam, no. 3, 193-195 (1982).
- (3) Minichelli, D.; De Pretis, A.; Ricciardiello, F., "Characterization of Raw Material used in the ceramic industry", Interbrick, no. 6, 17-20 (1988).
- (4) Enrique, J.E.; Amorós, J.L., "Materias primas para la fabricación de pavimentos y revestimientos cerámicos", Técnica Cerámica no. 91, 119-130 (1981).
- (5) Amorós, J.L.; Blasco, A.; Enrique, J.E.; Beltrán, V.; Escardino, A., "Variables en la compactación de soportes cerámicos de pavimento y revestimiento", Técnica Cerámica no. 105, 792-812 (1982).
- (6) Beltrán, V.; Bagán, V.; Sanchez, E.; Negre, F., "Características técnicas de las arcillas utilizadas para la fabricación de pavimentos y revestimientos cerámicos en pasta roja", Técnica Cerámica, 164, 280-287 (1988).
- (7) Bastida, J.; Beltrán, V., "Arcillas cerámicas de la provincia de Valencia", Bol. Soc. Esp. Cer. Vidr., 25 [4], 321-235 (1986).
- (8) Escardino, A.; Enrique, J.E.; Ramos, E., "Arcillas cerámicas de la Región Valenciana. II. Estudio 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).
- (9) Amorós, J.L.; Escardino, A.; Beltrán, V.; Enrique, J.E., "Quality control in tile production", Interceram, 33 [2], 50-54 (1984).
- (10) "Controles de fabricación de pavimentos y revestimientos cerámicos", Enrique, J.E.; Negre, F.; Blasco, A.; Beltrán, V., Ed. A.I.C.E. (1988).