TECHNICAL CONSIDERATIONS ON PORCELAIN TILE PRODUCTS AND THEIR MANUFACTURING PROCESS

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ACADEMIC BACKGROUND

- *Degree in Chemistry from the University of Valencia.*
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Dr. Sánchez has participated as senior researcher in over 50 R&D and Technology Consultancy projects conducted at the Instituto de Tecnología Cerámica, funded by ceramic tile manufacturers, frit and glaze producers, machinery builders for the ceramic industry, brick and roofing tile manufacturers, etc., as well as by public bodies belonging to the Valencia Regional Government, Spanish Government and European Union.

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Dr. Sánchez has delivered over 20 courses on subjects relating to ceramic technology both at ITC and at different companies in Spain and abroad.

ABSTRACT

This paper first seeks to clarify, from a technical point of view, the terminology used to define the different types of products currently included under the term porcelain tile. This requires briefly reviewing the historical evolution of the product from its appearance to the present day.

The second part analyses product performance (mechanical strength and toughness, stain resistance, whiteness and colour development, and frost resistance) and discusses how performance can be achieved through appropriate fired tile microstructure. It is also noted that strict control of the raw materials, process variables and green microstructure are needed to achieve these properties. On the other hand, the origins and solutions to some of the problems associated with porcelain tile manufacturing are examined, such as lack of pressing powder compressibility, segregation of mixtures of coloured powders and difficulty of polishing.

Finally, in view of the porcelain tile trend toward increasingly perfect reproduction of natural stones in recent years, some possible future R+D+I (Research+Development+Innovation) lines relating to product design and manufacturing technology are outlined.

1. INTRODUCTION

Porcelain tile production has witnessed remarkable growth in the last five years, partly due to the parallel growth of the ceramic tile industry worldwide, but especially to the significant effort of machinery builders and frit and glaze producers to diversify the decoration of a product that was originally unglazed.

According to the latest available data [1], Italian porcelain tile production in 2000 duplicated that of 1995. The forecasts for 2001 indicate that Italian porcelain tile production, Italy being the world's top porcelain tile producer with 50% market share, could reach 40% of total Italian ceramic tile production, equal to almost 300 Mm^2. This spectacular growth is largely the result of the powerful advance of glazed porcelain tile in the market, a product that could easily end up exceeding 60% of total Italian porcelain tile production in 2001.

If we analyse the evolution of the Spanish sector [1], the situation is somewhat different because although growth has been steady, it is not of such significant magnitude as that experienced by the Italian sector, although the installed spray-dried powder production capacity suggests greater potential growth in coming years. At the moment in Spain, porcelain tile accounts for just 6% of total ceramic tile production. The Spanish sector appears to be awaiting the commercial evolution of the product, presumably before taking off as regards production.

Independently of the existing differences between the two major world producers of porcelain tile, the reality is that today notable research efforts are being devoted to this product, with regard to material innovation as well to improving the manufacturing process, clearly demonstrating not just its current importance, but also its promising future.

This paper seeks on one hand to review the historical evolution of the product, from its origins to the current situation, since it can frequently be observed in the literature that porcelain tile is believed to be a product with hardly any historical tradition and just a few decades behind it. As we will see on looking backward, its origins date back to much more distant times.

In the second place, it is sought to shed some light on the confusing and ambiguous terminology around porcelain tile in general, and on the qualifier "porcelain" in particular, undoubtedly driven by the enormous dynamism of the product, with ceaseless changes in production processes and decorating techniques. With this terminology, the suitability or unsuitability will be discussed of certain qualifiers used to identify given types of ceramic tiles covered generally by the term porcelain tile.

The relation will subsequently be analysed between porcelain tile microstructure and performance, in particular as regards its mechanical properties, stain resistance, whiteness and colour development. Some of the problems associated with its manufacturing process will also be discussed, such as the lack of powder compressibility, demixing and segregation of the agglomerates during handling, and the difficulty of polishing the product.

Finally some possible future R+D+I lines relating to product innovation and manufacturing technology will be outlined, designed, just as latest market trends show, to achieve enhanced and more varied reproduction of natural stones.

2. HISTORICAL EVOLUTION OF PORCELAIN TILE

For lack of a more precise definition, to be discussed below, we can define porcelain tile as an impervious ceramic tile (i.e. without or practically without apparent porosity), glazed or unglazed, white or coloured by adding pigments to the starting composition.

Based on this definition we can find certain historical precursors of ceramic tiles exhibiting great similarities with the product currently known as porcelain tile.

A first evolutionary line takes us to England in the mid XIXth century. Specifically, around 1850-1860, the English company Minton, maker of "encaustic" or inlaid tiles introduced dust pressing to form products based on a French patent, quickly replacing plastic pressing. However, the product was manufactured at a low temperature, so that its porosity was high [2,3].

At the same time another English firm, Maw and company, which specialised in mosaics, started manufacturing tesserae, also doing so by dust pressing, but in this case with low porosity (water absorption below 3%), so that it was necessary to increase the firing temperature. The material was also coloured in mass, using colouring oxides for this purpose. This product should be considered as one of the historical precursors of today's porcelain tile. This product line was followed by other prestigious English manufacturers, such as Pilkington, and much later on by Johnson Tiles, amongst others.

This product philosophy was adapted by a businessman from Reus, Miguel Nolla y Bruixet, who in 1860 founded the factory Mosaicos Nolla, S.A, at Meliana (Valencia) [2-5]. The manufacturing process incorporated the English technology for manufacturing low porosity, body-coloured tesserae. The length of their sides did not exceed 7.5 cm, the most common being those of 5x5 cm. Production was enormous, ending up with thousands of workers. Current testimonies of Nolla mosaic are abundant, particularly in the centre (New District) of the city of Valencia (Figure 1), although the product was installed in many parts of the world, as it was the only factory manufacturing a material of such characteristics. By way of example, Nolla mosaic is also found at the Kremlin on Moscow's Red Square.

Figure 1. Example of Mosaico Nolla flooring in a house of the New District of the city of Valencia.

Company decline began toward the end of the XIXth century, when hydraulic flooring was developed, which was much cheaper though with lower performance than ceramic tesserae. Nevertheless, company activity continued up to 1960.

In a recent study, Botella et al [6] characterise seven Mosaico Nolla tesserae, selected from the ceramic museum of Manises. These researchers conclude that it is a product made using compositions of a kaolinitic nature with abundant free quartz. In the coloured samples the iron oxide content is high, as is that of manganese oxide. Furthermore, the technological tests allow establishing that it is a highly sintered floor tile, which means high density and scarce apparent porosity (water absorption between 2-3%). The starting composition was quite likely formulated almost exclusively by siliceous kaolins, such as those beneficiated in the towns of the Northwest of the Valencia Region, such as Llíria, Benaguacil or Sot de Chera.

The second historical porcelain tile precursor relates to the German clinker [7]. The term "klinker" has its origin in the clean "clink" that is heard on striking the product that has been fired to sintering, and comes from the Dutch word "klinken". In general, a clinker is a brick made from more or less fluxing clays that densify during firing with or without additives, and is fired until fully sintered, i.e., disappearance of apparent porosity. In practice however, water absorption of the product was rarely less than 2%. Clinker production began in Holland toward the second half of the XVIIIth century and quickly spread to Germany [8]. Clinkers were used for foundations and interior and outside walls subject to high stresses, for bearing columns and in general wherever special resistance was needed against aggressive agents (physical or chemical) and against mechanical surface stresses.

After the second and third decade of the XIXth century onward, building products were in high demand, in particular by the powerful, expanding German chemical industry. This need, together with the already existing brick clinker manufacturing technology, led to the appearance of a type of tile known as clinker or fine clinker, typically made by extrusion and generally unglazed, with water absorption below 3% (although always exceeding 1%), in pieces up to 24 cm long. This product should be considered as the second porcelain tile precursor.

Later on in Italy, after the Second World War, the product began to be imitated. It became thinner, was formed by pressing, coloured in mass, and made in sizes up to 10x10 cm. The product was however used in industry but hardly in the home. Some examples of manufacturers of this product are companies that were located outside the Sassuolo district, such as Ceramica Vaccari (Genoa) or Ceramica Appiani (Treviso). This situation was kept until approximately the beginning of the 70s [9].

In the Sassuolo district, the product appeared toward the end of the 70s, made by certain manufacturers such as Casalgrande Padana, Nordica, Mirage, Flaviker and Graniti Fiandre, which saw potential commercial success in the product, at a time when most companies were hastily changing over from red to whiteware production, installing single-firing lines at their facilities. This signalled the commencement of the great technological upgrading of the sector, with the introduction of roller kilns. Pressing was optimised (hydraulic presses), the product was polished and its range of decorations grew. Modern porcelain tile was born in Europe.

The product appeared in Spain much more recently, when it had already been manufactured for a decade in Italy. Specifically, in 1988 Pamesa started producing porcelain tile, followed by Porcelanatto in 1989 and later on, in the 90s, by the rest of the companies.

3. TERMINOLOGY

We have already mentioned that porcelain tile adopted its current physiognomy (size, thickness, surface finish by polishing, etc.) in Italy in the 70s. It is in fact at that time when, coinciding with the birth of the product, the term porcelain tile was coined.

However, over these more than 25 years of existence, the product has undergone spectacular transformation, the most significant probably relating to its surface decoration, i.e., the upsurge of glazed porcelain tile in the last five years. Since then the product has exhibited great dynamism, with new decorating techniques continually appearing, while modifications in production technology make it necessary to constantly invent terms to identify these evolving variations of the product. The problem stems from the fact that terms are coined from a purely commercial point of view, without due reflection and technical rigor, which can easily lead to confusion and ultimately misunderstanding.

Thus, in these last few years terms have rapidly appeared such as "technical" porcelain tile to refer to an unglazed porcelain tile (as if the glazing operation involved no technical difficulty), "red" porcelain tile [10], to indicate that the product body has been made from clays with a high iron oxide content, and hence with a red fired colour, and more recently "semi-technical" porcelain tile [11] to define, rather unclearly, a product that for various reasons does quite reach "technical" porcelain tile performance levels.

At this point, and in view of the evident existing confusion, it is useful to review the original term and its possible implications. The Spanish term for porcelain tile, "gres porcelánico" consists of the noun "gres" (stoneware) qualified by the adjective "porcelánico" (porcelain). The Dictionary of Ceramics of the well-known Institute of Materials of London gives a good definition of both words [12].

The dictionary defines gres ("stoneware") as a generally glazed ceramic product "which, though dense, impermeable and hard enough to resist scratching by a steel point, differs from porcelain because it is more opaque and generally only partially vitrified. It may be vitreous or semi-vitreous. It is usually coloured grey or brownish because of impurities in the clay used." On the other hand, "porcelánico", as having a porcelain quality, refers to a totally vitrified ceramic product, which is impervious (even without glazing), white or artificially coloured, translucent (except when it is very thick) and resonant. In the United Kingdom the term is defined based on the composition, indicating that the mixture used is of the feldspathic type (kaolin-quartz-feldspar). Other consulted literature sources coincide with the foregoing definitions [7,13].

As can be observed, the adjective "porcelain" basically qualifies three aspects of the definition of "gres": total absence of porosity (at least apparent) on dealing with an impervious product, of a white fired colour or coloured artificially, and made using a composition based on the three-component mixture kaolin-quartz-feldspar.

As a result, we can define "gres porcelánico" (porcelain tile) as a fully vitrified, impervious ceramic tile, glazed or unglazed, whose fired body is white or artificially coloured, and which is made by using a composition based on a mixture of kaolin (or kaolinitic clays) quartz and feldspar. In practice, this definition must be compatible with the ISO standard classification for ceramic tiles, as a result of which the qualification of fully vitrified can be understood as having water absorption less than 0.5%.

Therefore, having established the basis of the product's definition, we need to interpret the uses currently being made of the qualifying term porcelain. Thus, the term technical porcelain tile lacks all logic and rigor (and hence so does semi-technical porcelain tile), since there is no type of relation between non-technical and glazed. In any event, it would appear to be appropriate to identify whether the porcelain tile is glazed or not (as occurs with any type of tile), since the definition of "gres" and porcelain indicate that the product may or may not be glazed.

As far as "red" porcelain tile is concerned, without being in any way critical of the quality of a product of very low porosity, formulated entirely with Spanish red clays, the qualifier porcelain should not be applied either, since it is not a white-firing product coloured by adding pigments, and has not been made using the basic porcelain composition mentioned previously. Red stoneware of low or very low water absorption would probably be a more appropriate term.

Therefore, with a view to maintaining the prestige of the product in its future course in world markets, it is necessary to try and maintain terminological accuracy at the same time as the performance features associated with the definition of the product (performance features to be discussed below). Only thus, shall we be able to transmit and maintain the identity of the product without deterioration of its image and quality.

4. PORCELAIN TILE MANUFACTURE: AN ADVANCED CERAMIC PROCESS

Figure 2 schematically illustrates the porcelain tile manufacturing process. The manufacture of a high performance product such as porcelain tile, through rigorous microstructural control requires high quality raw materials and a highly technologised production process. These characteristics are closer to advanced or high-tech ceramic production processes than to those used in manufacturing traditional ceramic products.

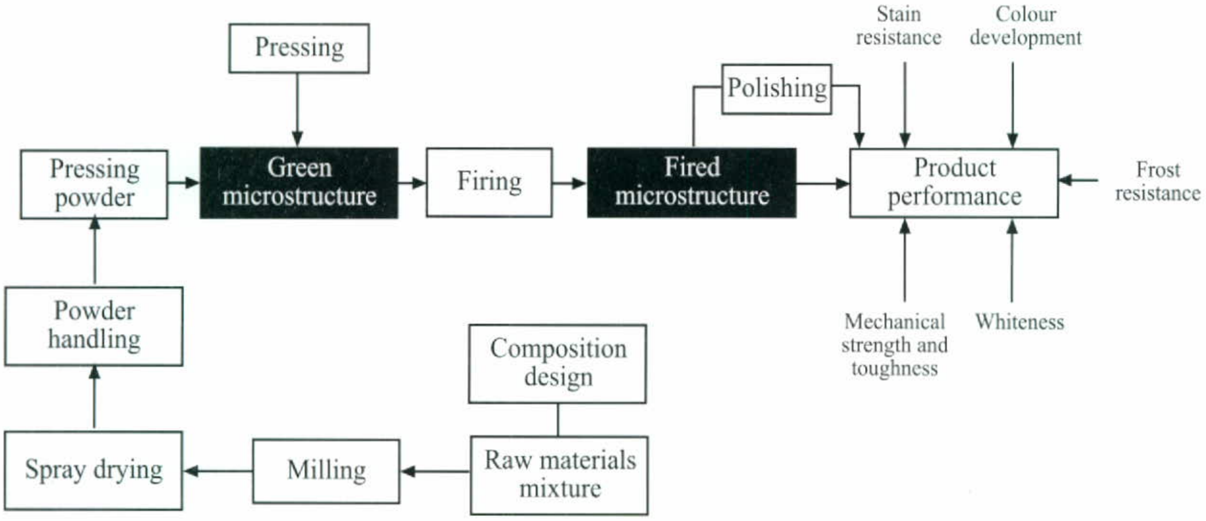


Figure 2. Scheme of the porcelain tile manufacturing process and relation between the process stages, tile microstructure and product properties.

Product requirements are as follows: high degree of whiteness, good colour development, high mechanical strength (and toughness) and high stain and frost resistance.

Attainment of these objectives is basically related to producing the appropriate microstructure in the fired tile. Although this aspect will be dealt with in further detail below, to start with we can say that the microstructure should be characterised by being free or practically free of apparent porosity, with a minimum closed porosity, in turn made up of perfectly isolated, small-size pores (10 μm or smaller) [14]. The solid fraction, consisting of a glassy matrix, should contain sufficient reinforcing material (crystalline phase) to enhance the mechanical properties of the matrix. Finally, the relation between the glassy phase and the crystalline phase also noticeably affects the aesthetic characteristics of the product, such as whiteness and colour development.

It would not be possible to achieve this fired microstructure without previously producing an appropriate microstructure in the formed tile. Together with this condition, the selection of the firing variables is a basic aspect involved in attaining this objective. During firing beside other transformations, tile densification occurs, which in the case of porcelain tile takes place by a liquid phase sintering mechanism [15,16]. In this mechanism, liquid phase viscosity plays a decisive role in establishing the rate of the densification process, of crystalline phase dissolution and of the devitrification of new phases.

Suitable microstructure in the green tile refers to a tile whose porosity consists of small-size pores with a relatively narrow size distribution. Moreover, this microstructure should be free of deformed or incompletely broken up granules, since these would act as discontinuities and heterogeneities that would diminish performance, not just of the formed tile, but even of the final product [14,17]. Producing this ideal green microstructure depends on the selection of certain high quality raw materials free of impurities, by rigorous control of the milling and spray-drying operation to produce appropriate pressing powder, and finally a pressing program that enables reproducing this microstructure throughout the whole tile, independently of its size and across all the formed tiles.

4.1. STARTING COMPOSITION DESIGN AS A FUNCTION OF PRODUCT REQUIREMENTS

Figure 3 presents a flow diagram of the formulation criteria to be considered in the design of an unglazed porcelain tile composition (the requirements of the glazed porcelain tile body are less demanding).

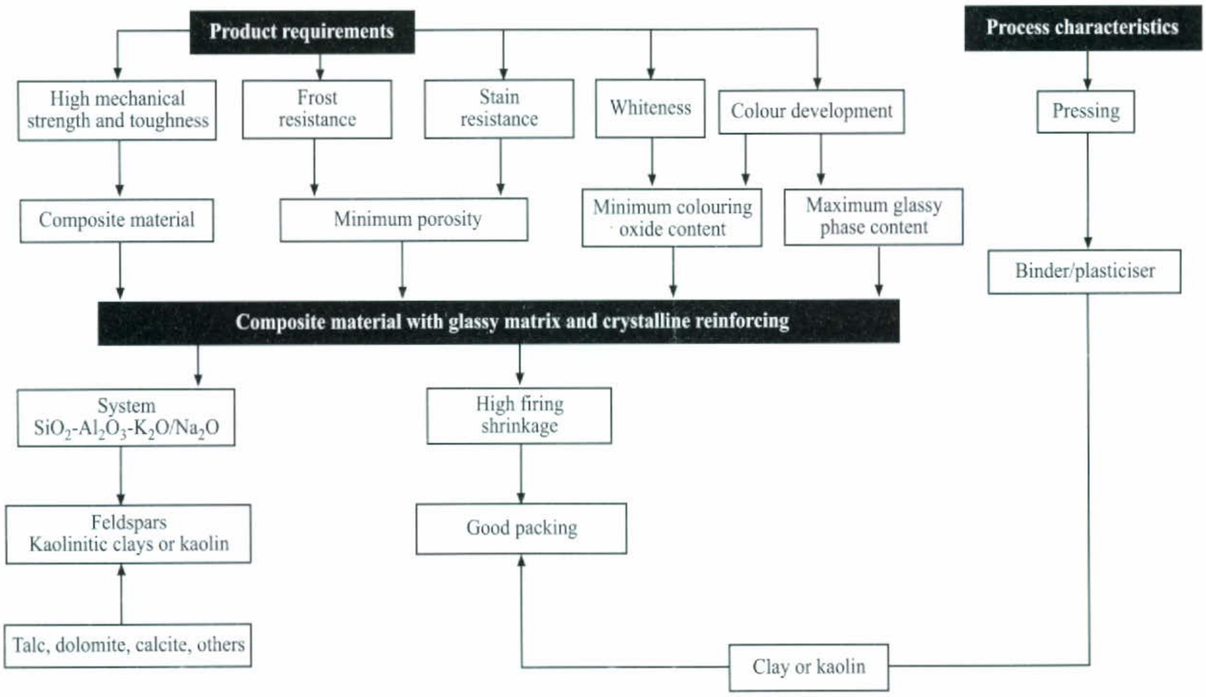


Figure 3. Flow diagram of the design of a porcelain tile composition.

As can be observed, product performance can only be attained by designing a material consisting of a glassy matrix that assures the reduction of porosity in a fast firing cycle at relatively low temperatures, using strengthening of a crystalline nature that reduces the brittleness of the glassy matrix. Ceramics offer infinite possibilities for designing materials made up of the foregoing characteristics. One of the most accessible and economic combinations is the one based on the ternary system $SiO_2/Al_2O_3/M_2O$, M_2O being a fluxing alkaline oxide, just as those supplied by sodium or potassium feldspar. In practice the incorporation of sodium feldspar is usually preferred, owing to its lower melting temperature.

On the other hand, tile forming by pressing requires a sufficient contribution of colloidal particles to encourage packing and cohesion (binding effect) of the larger-sized particles contributed mainly by the non-plastic material. In practice these colloidal particles are introduced in the form of kaolinitic clays with low iron oxide contents and kaolins.

On occasions, with a view to favouring the formation of eutectic mixtures with a low melting temperature, compounds are added which contribute alkaline-earth oxides (CaO and MgO), such as calcite, dolomite, talc or wollastonite.

This type of compositions allows thermal treatment at moderate temperatures (around 1200°C), to produce a material made up of a glassy matrix of composition SiO_2-Al_2O_3-M_2O, abundant silica (quartz) without dissolving, and the crystallisation of small proportions of mullite (Figure 4).

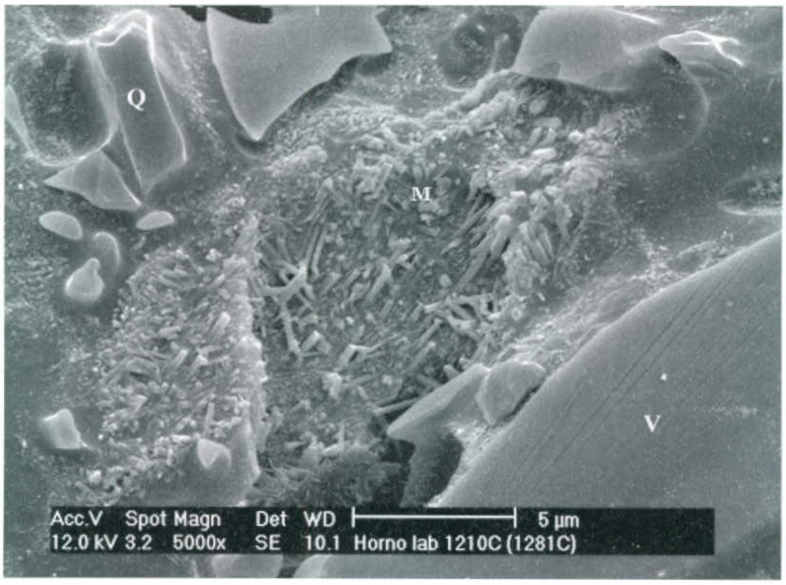


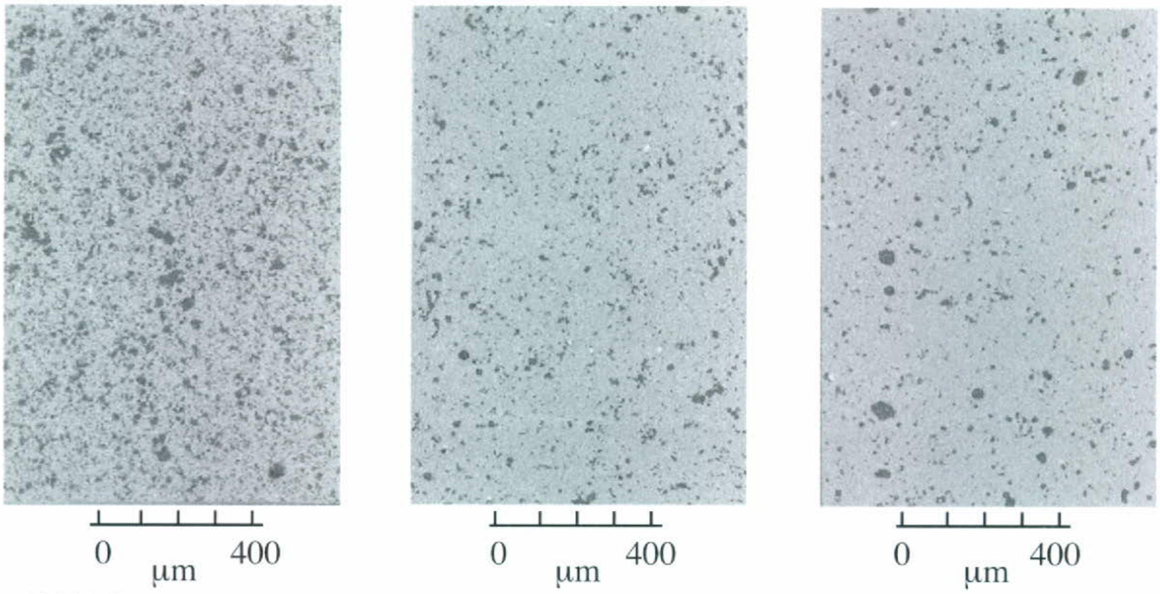
Figure 4. Fracture surface etched with acid of an industrial porcelain tile fired at 1210°C. It shows the glassy matrix (V), undissolved quartz (Q) and mullite crystals (M).

Thus in general, porcelain tile compositions are formulated based on a ratio approaching 1:1 of plastic material (kaolinitic clay and kaolin) and non-plastics (mainly sodium feldspar, sodium-potassium feldspar and quartz). The main differences between the compositions for manufacturing unglazed and glazed porcelain tile is the exclusive presence of imported clays (because of their lower impurities content and greater plasticity) and the possibility of introducing kaolin in the former case. Furthermore, the non-plastic raw materials (feldspar and quartz) used in the unglazed product are of higher quality (lower impurities content), in order to achieve a high degree of whiteness, good colour development and minimum final porosity.

4.2 RELATION BETWEEN PORCELAIN TILE GREEN AND FIRED MICROSTRUCTURE

Porcelain tile densification occurs by a sintering mechanism with the presence of liquid phase. As described in the literature [15,16], on increasing firing temperature porosity decreases and pore size growth takes place as a result of the progressive elimination of the smallest pores. At higher temperatures, the proportion of liquid phase rises while viscosity decreases, enabling removal of pores of growing size. The initially communicating porous system loses connectivity with sintering advance, and closed porosity starts to form.

At high temperatures, apparent porosity disappears and the evolution of the porous texture needs to be followed by observation of polished cross sections of the pieces. Figure 5 shows that at temperatures around 1200°C, raising temperature reduces tile porosity until reaching maximum densification (T_{max}), which is around 1220°C in this case. A subsequent rise in temperature causes effective viscosity of the tile to decrease, making it more deformable, while gas pressure in the pores exceeds capillary pressure, causing the tile to expand. The optimum firing temperature of this type of product is in fact maximum densification temperature (T_{max}), and the starting composition should be such that this temperature exceeds that at which apparent porosity disappears. Otherwise, the fired product would contain open pores, as is the case of stoneware floor tile in which red clays are used as raw materials [18].



1200°C 1220°C 1240°C

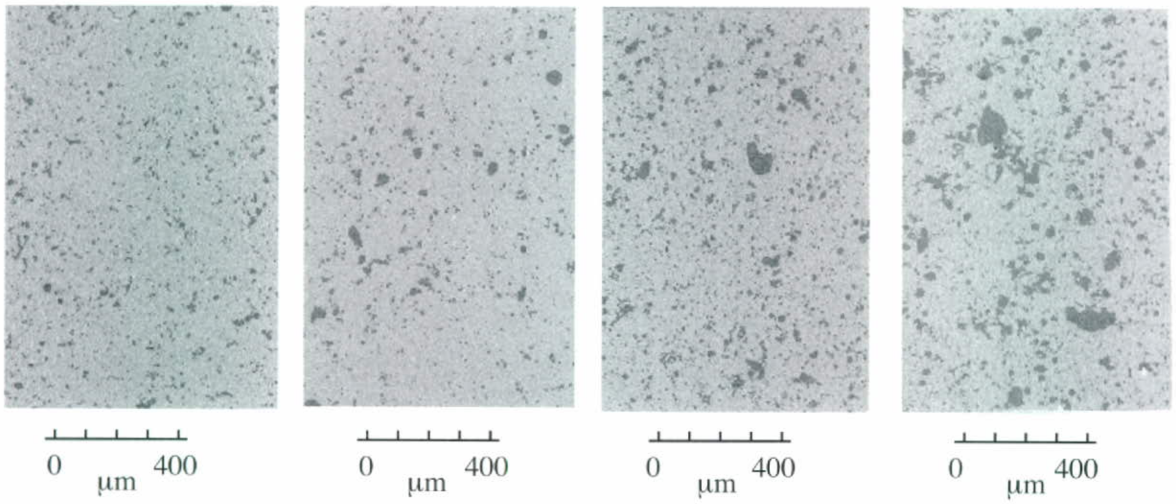
Figure 5. Polished surface of porcelain tiles made from a standard composition.

4.2.1 Effect of spray-dried powder particle-size distribution (PSD)

In the literature the effect of porcelain tile composition PSD on the sintering process and on the microstructural characteristic of the fired pieces is analysed. For this, Orts et al. [16] compare the behaviour during firing of four porcelain tile compositions milled for different times to obtain different mill oversizes.

These researchers conclude that, at the same pressing variables, with a greater large particle fraction in the composition (higher reject at 40μm or smaller degree of milling), less porous pieces are produced, however containing larger pores. On the other hand, with more vigorous millings (smaller reject at 40μm), more porous pieces are produced, but the pores are smaller. These results agree with the literature [19] and confirm that particle size is directly related to pore size in the green packing.

The appearance of the porous texture of tiles fired at maximum densification temperature (T_{max}), and then polished, made from the four previously mentioned compositions, is shown in Figure 6. The figure also includes the mill reject at 40μm (R), maximum densification temperature (T_{max}), and final porosity (ε). It can be observed that as the reject at 40μm rises (degree of milling decreases), more porous pieces are produced with larger-size pores. These findings confirm that pore size growth occurring during sintering depends on pore size in the green tile, so that fired tile end porosity will depend more on green tile pore size than on pore volume.



R1=1.6%	R2=2.6%	R3=6.1%	R4=11.7%
T_{max}=1224°C	T_{max}=1232°C	T_{max}=1240°C	T_{max}=1245°C
ε=9.9%	ε=10.1%	ε=10.4%	ε=11.0%

Figure 6. Cross sections of pieces fired at Tmax made from porcelain tile compositions with different milling rejects (R1 to R4).

4.2.2 Effect of pressing variables

The effect of pressing variables (pressure and moisture content) on green porcelain tile microstructure has been described in the literature by various authors [17,20]. Figure 7 attempts to summarise this effect by plotting the mean pore diameter of porcelain tile test specimens formed at different pressing pressures using spray-dried powder with three different moisture contents. It can be observed that raising pressing pressure and powder moisture content lowers mean pore size, which facilitates the subsequent sintering process. In a certain way with regard to green tile microstructure, the effect of raising powder pressure and/or moisture content is similar to that of decreasing particle size, set out in the previous section.

Thus increasing pressing pressure facilitates tile densification, since it increases the energy contributed for deforming and breaking up the agglomerates. Raising moisture content leads to greater compressibility of the powder, by decreasing agglomerate yield pressure and reducing interparticle friction forces [21,22].

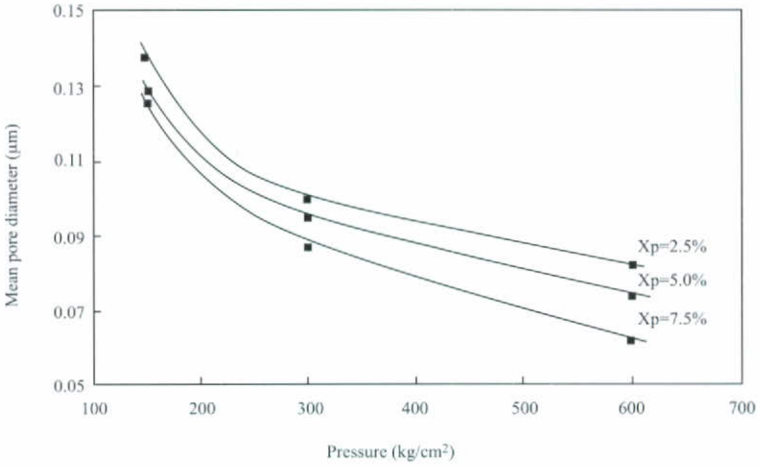


Figure 7. Effect of pressing variables (pressure and powder moisture content) on porcelain tile mean pore size.

4.3. RELATION BETWEEN PORCELAIN TILE FIRED MICROSTRUCTURE AND CERTAIN PROPERTIES

4.3.1 Mechanical strength and toughness

Porcelain tile is a material with high mechanical strength in the field of ceramic tiles, largely due to its glass-ceramic nature. Material failure is by brittle fracture, which can be modelled by linear fracture mechanics. The Irwin approach is one of the most widely used models for determining the mechanical strength of brittle materials [23]:

$$\sigma_R = \frac{1}{Y}\frac{K_{IC}}{\sqrt{a_c}}$$

- Where σ_R is mechanical strength, Y is a geometric factor that depends on the way of applying the load and tile geometry and, lastly, a_C represents critical flaw size, i.e., the flaw size at which brittle fracture of the material takes place. As this expression shows, to design a ceramic material with high mechanical strength it is necessary to produce good toughness and rigorously control the microstructure (flaw size) of the product.

- The improvement of porcelain tile mechanical properties is an issue of growing interest in the literature [24,25]. Recently some authors have addressed the role of residual crystalline phase (quartz) in strengthening the structure of the material. Leonelli et al. [24] postulate, based on the similarity of porcelain tile microstructure to that of porcelain, that in porcelain tile mechanical strength two mechanisms are involved which contribute to increasing toughness. In the first place, the quartz crystals provide resistance to crack propagation by microcrack formation. This mechanism is easily visible in the microstructure of an indented tile, as a ramification of the crack in the area where it impacts a quartz grain (Figure 8a). In second place, a crack deviation mechanism occurs in the vicinity of quartz grains (Figure 8b).

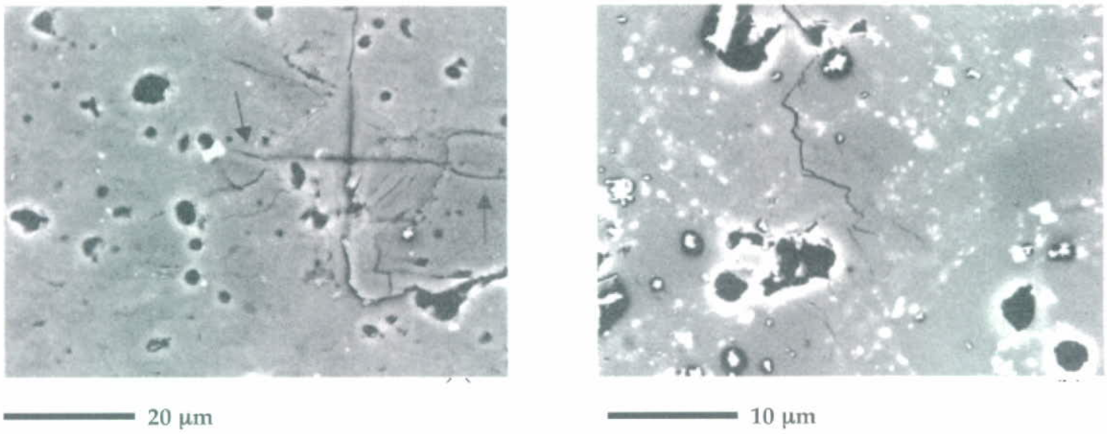


Figure 8. Strengthening mechanisms of residual quartz grains in porcelain tiles: a) by microcrack formation and b) by crack deviation (Source: ref. 24).

A recent work [26] has highlighted the role of mullite in reinforcing the porcelain tile glassy matrix. The study indicates that on raising the kaolin (or kaolinitic clay) content in the starting composition, the mullite proportion is increased in the fired pieces, which leads to an important rise (almost 40%) of mechanical strength. However, the strengthening effect peaks at a kaolin content around 40% (14% mullite) and then decreases. The presence of this maximum value, very common in other ceramic composites [27], is based on the existence of two simultaneous but opposing effects, as Figure 9 shows. Thus, increasing the mullite content raises toughness (K_{IC}), while the population and size of the microstructural flaws (a_C), associated with the presence of this crystalline phase in the glassy matrix, also increase simultaneously. This last effect can be observed in the micrographs included in Figure 9, corresponding to pieces made with compositions containing 35% and 65% kaolin (12.1% and 25% mullite).

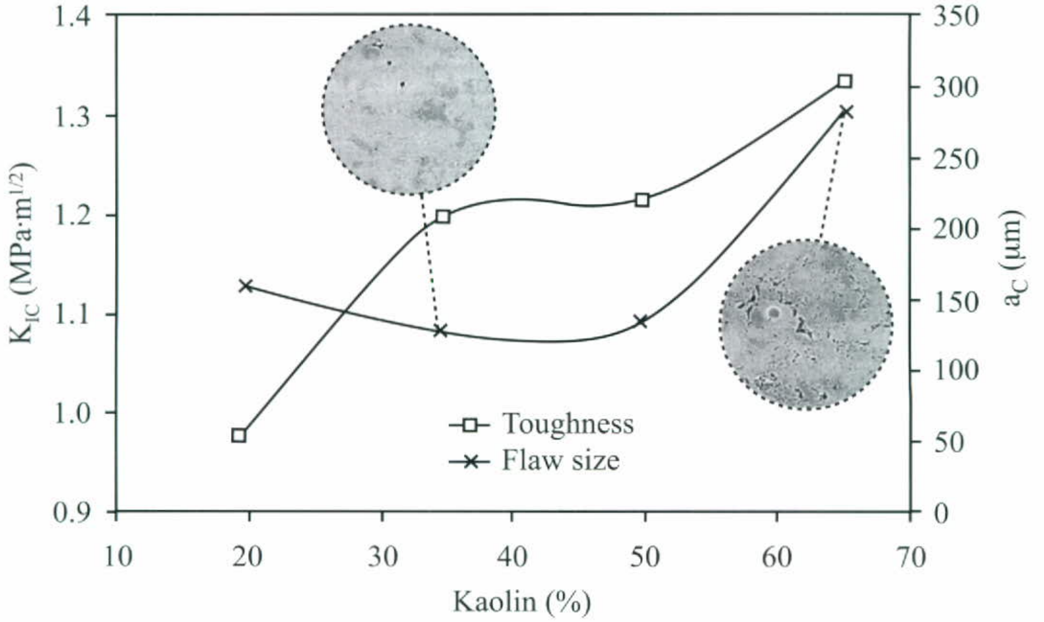


Figure 9. Variation of toughness (K_{IC}) and critical flaw size (a_C) in the fired porcelain tile as a function of the kaolin content in the starting composition.

4.3.2 Stain resistance

To analyse the relation between tile porous texture and stain resistance, Figure 10 plots the variation of cleanability and stain retention with firing temperature of tiles made with a standard porcelain tile composition. This property was evaluated by colorimetry. Thus, stain resistance (stain retention) was determined based on the change in colour (ΔE) of a polished porcelain tile surface which was stained and then wiped clean with a damp cloth. To evaluate cleanability, the same stained pieces were subsequently cleaned in a mechanical device (using a conventional cleaning agent), determining the ΔE between the original surface and the surface after the cleaning process.

The background of Figure 10 shows the microstructure of the polished pieces fired at $T<T_{max}$ (maximum densification temperature), $T=T_{max}$ and $T>T_{max}$. It can be observed that stain retention decreases on increasing firing temperature, minimising at T_{max}. This decrease is due to the reduction in tile porosity, while the increase found at $T> T_{max}$ is because of tile bloating caused by the pressure of the gases trapped in the pores, as indicated previously.

With regard to cleanability, ΔE decreases (cleanability increases) until reaching T_{max} and remains constant at higher temperatures, in the studied range. The fact that ΔE does not increase above T_{max} is because when the tile expands, porosity rises by increasing pore size and not the number of pores, and it is easier to remove material that has entered large pores than that which has entered small pores.

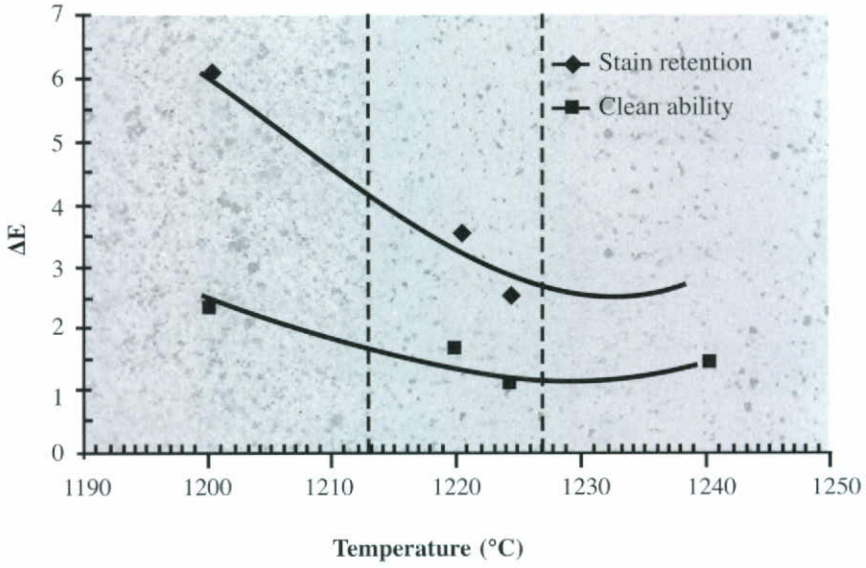


Figure 10. Standard porcelain tile composition. Variation of dirt retention and cleanability with firing temperature in polished pieces.

4.3.3 Whiteness

The whiteness of the fired product depends to a great extent on the starting raw materials composition. Figure 11 shows that reducing the quantity of Fe_2O_3 and TiO_2 in a standard porcelain tile composition raises the degree of whiteness in the fired product (co-ordinate L* increases and co-ordinate b* decreases). The figure also shows that the porcelain tile working temperature area (marked with a circle) practically coincides with the product's minimum whiteness as a result of the colouring effect of FeO with its introduction in the arising glassy phase. According to Zhou and Weissman [28], the incorporation of iron in the glassy phase is the main cause of the loss of whiteness in porcelain, since at a certain iron oxide content in the composition, mullite, which could accommodate the same quantity of iron as the glassy phase, does not exhibit the same change of colour as the glassy phase.

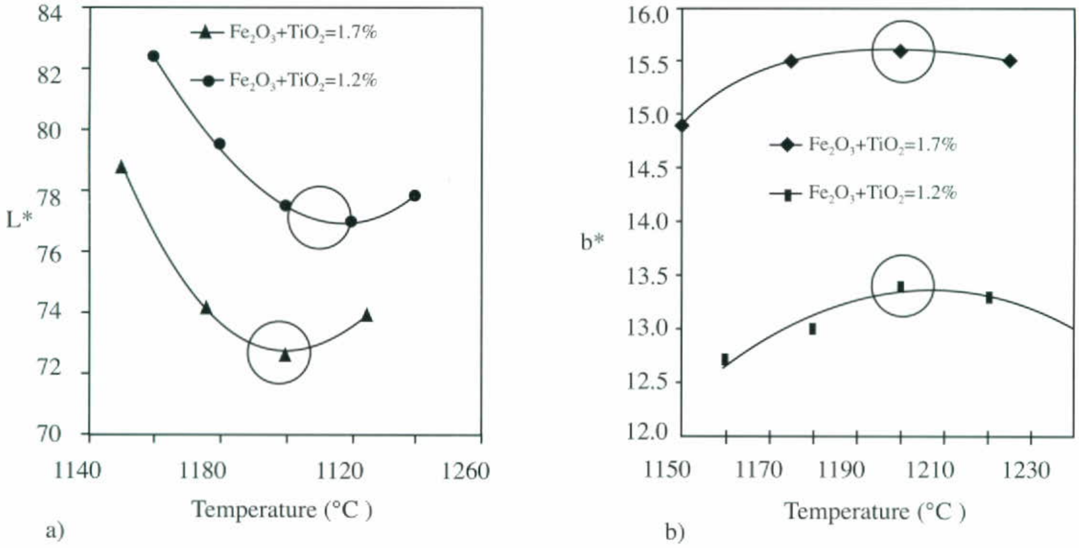


Figure 11. Variation of co-ordinate L (a) and b* (b) with temperature for two porcelain tile compositions with different contents of colouring impurities Fe_2O_3 and TiO_2.*

At the same chromophore impurities content, the final whiteness of the product depends on the nature and proportion of the phases that develop during firing. Recently Sánchez et al. [26] confirmed the existence of a good correlation between whiteness (co-ordinate L*), yellowness (co-ordinate b*) and the quantity of crystalline phases in the fired product (quartz+mullite), such that whiteness increases (L* increases) and yellowness decreases (b* decreases) as total crystalline phase content rises (Figure 12).

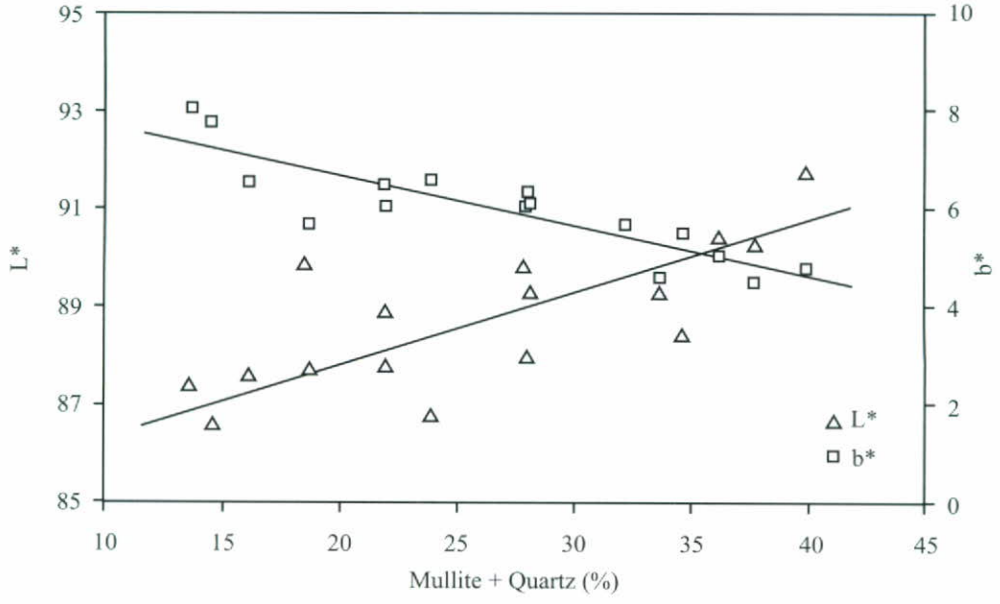


Figure 12. Variation of chromatic co-ordinates L and b* with crystalline phase content (quartz+mullite) in the fired tile.*

These results highlight the opacifying effect of the crystalline phases present in the glassy matrix. Though the differences in refractive index between mullite (1.67) and quartz (1.54) with regard to the glassy phase (around 1.62) are small, the presence of crystals of both compounds in the glassy phase is the main opacifying mechanism. On the other hand, owing to the low content in chromophore elements (iron and titanium) present in these crystalline phases, this opacification raises the whiteness of the tile (L* increases and b* decreases). The opacifying effect of the devitrified mullite is greater than that of the residual quartz because its particle size is much smaller.

4.3.4 Colour development

Just as whiteness, colour development in the coloured products depends, as some authors indicate [29], on the chromophore impurities content in the raw materials. The decrease in the proportion of this type of impurities generally means better colour development. However colorant strength is also related to the glassy phase content in the fired tile and even to the nature of this glassy phase.

Thus in general, increasing the proportion of glassy phase encourages colour development, since it reduces the opacifying effect of the crystalline phase. To verify this fact, the effect of the four basic ingredients of a standard porcelain tile composition (kaolin, quartz, sodium feldspar and potassium feldspar) on colour development was analysed. For this, raw materials practically free of impurities were used. Three industrial pigments were chosen: black, blue and red. For the sake of brevity only the results found with the black pigment have been included in this paper. Figure 13 plots the variation of chromatic co-ordinate L* of the porcelain tiles versus the quantity of each ingredient of a composition to which a standard amount of the black pigment was added.

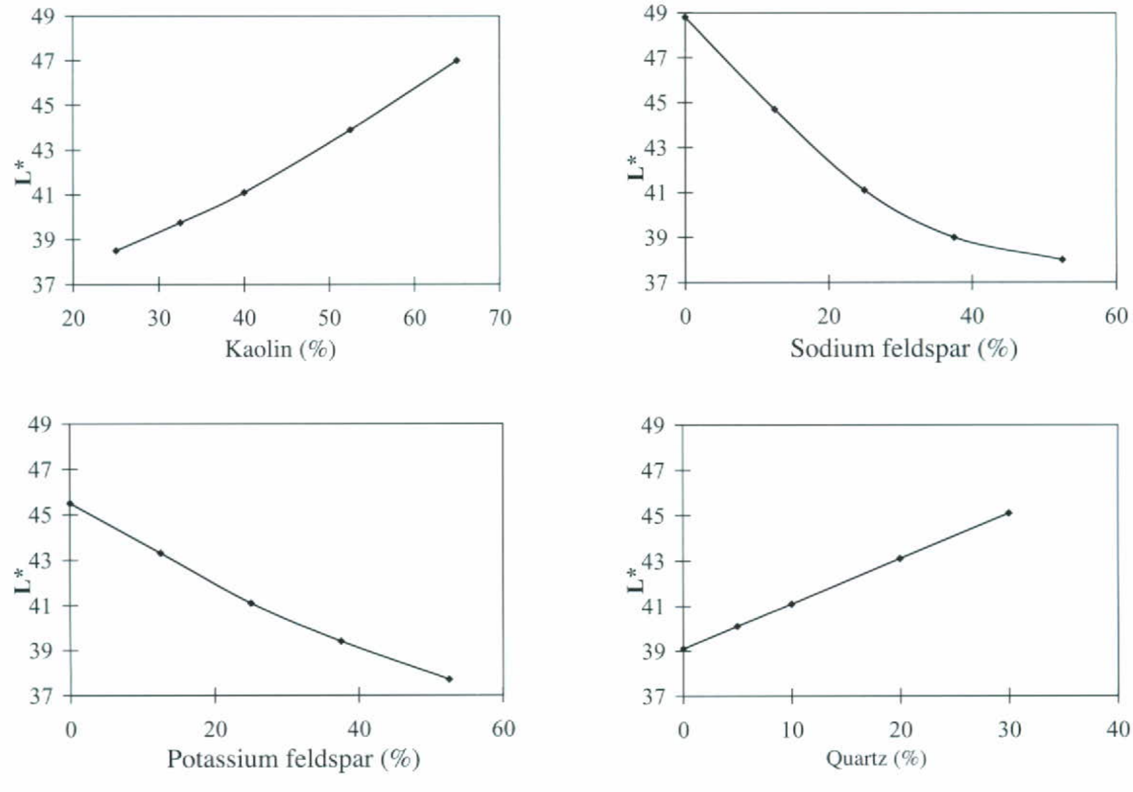


*Figure 13. Variation of chromatic co-ordinate L * of black porcelain tiles with the proportion of starting mixture ingredients: (a) kaolin, (b) sodium feldspar, (c) potassium feldspar and (d) quartz.*

It can be observed that kaolin, by favouring mullite formation, and quartz, given its scarce solubility in the melt, reduce the intensity of the arising colour (increase of co-ordinate L*), as a result of the opacifying (whitening) effect described in the previous section. In contrast, on increasing the feldspar content, colorant yield rises strikingly (L* decreases). Differences do not appear to be noticeable with regard to the nature of the feldspar (sodium or potassium), probably because the pieces were fired to maximum vitrification temperature, which involved using different temperatures in each case, but which enabled producing the same viscosity in the glass developed during sintering. Similar results were found with the other two pigments (blue and red).

5. CERTAIN PROBLEMS ASSOCIATED WITH THE MANUFACTURING PROCESS

5.1 LACK OF POWDER COMPRESSIBILITY

The pressing powder used in porcelain tile manufacture generally exhibits low compressibility, because:

Making a product with minimal porosity and appropriate colour development requires using compositions with a high proportion of feldspar, in other words minimising clay content, since this raw material is usually also the main contributor of impurities to the composition.

Intense milling of the composition to produce an appropriate microstructure in the green tile gives rise to narrow particle-size distributions (PSD), which are not very suitable for packing (section 4.2.1).

Figure 14 plots dry bulk density using porcelain tile compositions with different quantities of a practically quartz-free clay. The figure presents an ideal visualisation of packing with three different clay contents (the small and large spheres respectively symbolise clay and non-plastics particles). It can be observed that compactness peaks at a clay proportion around 33% by weight. At this maximum value, the clay particle content is sufficient to occupy most of the voids left by the non-plastics particles. Larger clay contents lead to an expansion of the structure, as shown in the scheme. These results are consistent with those found in the literature for binary mixtures of spherical particles [19,30], in which maximum packing density is generally found in a small/large particle volume ratio of 35/65. Porcelain tile compositions usually lie below this optimum.

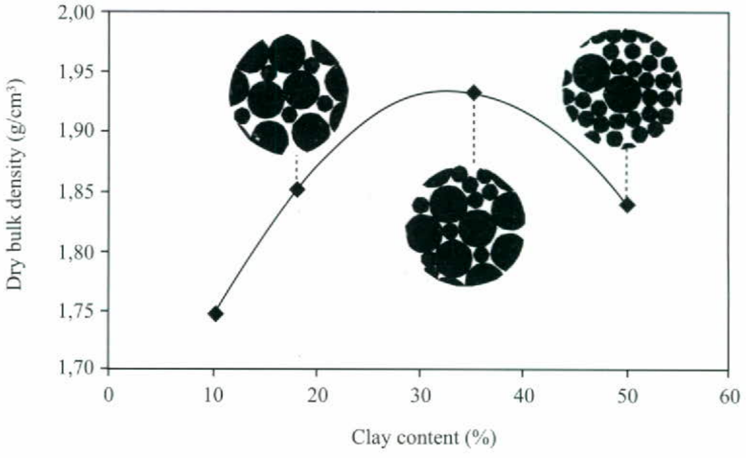


Figure 14. Variation of dry bulk density of porcelain tile compositions formed with different clay contents (also including the ideal packing model of bimodal spheres).

On the other hand, intense milling of the composition also reduces powder compressibility. The reason for this behaviour is the narrowing of the particle-size distribution that takes place as milling time increases (reducing the oversize). In a ball mill, narrowing PSD mainly means decreasing the size of the largest particles (>30-40 μm), mainly involving the non-plastics, since the clay particles hardly experience the milling action. Recently Sánchez et al. [30] showed this effect by studying the packing of binary mixtures of clay and feldspar. According to these authors, reducing feldspar particle size (more intense milling) decreases the size of the void (pore) available to lodge the smallest clay mineral particles, so that the packing expands and compactness diminishes. There is a minimum non-plastics:clay mineral size ratio, below which compactness is adversely affected (around 1:10).

Finally, the rise in pressure required to counteract inadequate powder compressibility for the foregoing reasons can cause problems during production, since this rise in pressure entails an increase in the elastic response (axial expansion) of the tile after pressing (Figure 15). According to some authors, the increase in axial expansion raises the risk of laminations and exfoliation during pressing, so that the pressing cycle is slowed down on requiring longer de-airing time [31,32].

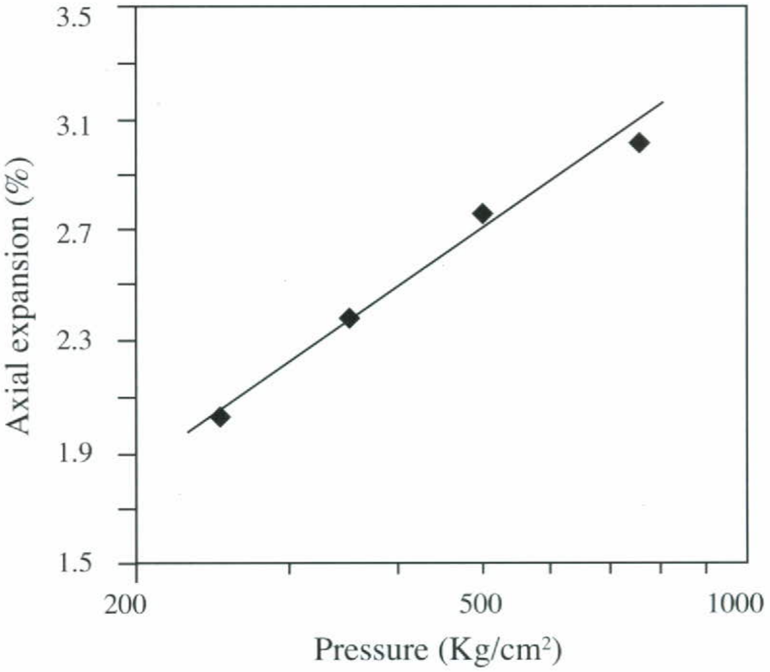


Figure 15. Variation of the axial expansion of the recently pressed tile with pressing pressure.

5.2 SEGREGATION AND DEMIXING

As powder flowability increases, its tendency to segregate also rises. If the agglomerates were the same size, with the other agglomerate characteristics being the same, there would be no possibility of segregating. However, small size variations among the agglomerates in a powder with high flowability can already cause segregation. Indeed as Figure 16 shows, segregation of an agglomerate powder can start at size ratios as small as 1.1, increasing exponentially with larger differences in size.

These size differences always exist in the manufacturing process and are especially evident when mixing coloured powders, frequently producing changes of appearance ("shades") in the final product. In fact it has been demonstrated that agglomerate segregation in a mixture of coloured powders can end up producing the same change of appearance in the final tile as an error in proportioning one of the ingredients [33].

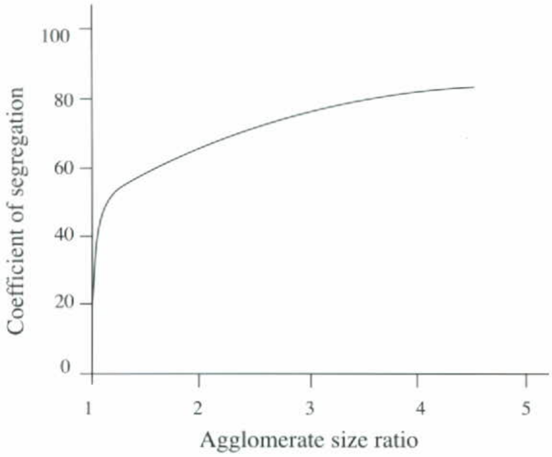


Figure 16. Variation of the coefficient of segregation with the agglomerate size ratio.

Segregation gives rise to demixing of the powder. For this reason, powders with high flowability mix and demix with great ease. Therefore, the only way of avoiding demixing (segregation) of a spray-dried powder in which size differences exist among the agglomerates is by minimising powder movement. Some actions which can be carried out in the production process with a view to reducing the problem of segregation are:

-Reducing, as far as possible, intermediate storage of spray-dried powder, in particular, of mixtures of coloured powders. The fall of powder during storage is a highly segregative process (Figure 17).

- Appropriately designing bins and hoppers[34]. This involves using feed systems fitted with flow dividers and have discharge angles that favour mass flow during bin discharge instead of funnel flow. Mass flow (Figure 18a) ensures homogeneous discharge, unlike funnel flow (Figure 18b) in which the centre part of the bin, richer in small agglomerates, empties first, followed by the parts close to the walls which contain a greater proportion of large agglomerates.

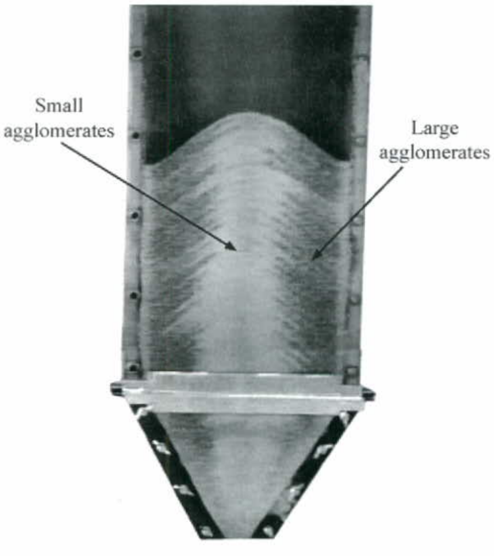


Figure 17. Segregation during bin filling with spray-dried powder of two colours: black agglomerates (large) and white agglomerates (small).

A proposal compatible with the foregoing considerations is that of using teleguided mobile hopper systems (provided hopper design is appropriate), as powder handling is reduced, the size of the batch is smaller and mixture preparation practically coincides (there is hardly any intermediate storage) with feed to the press.

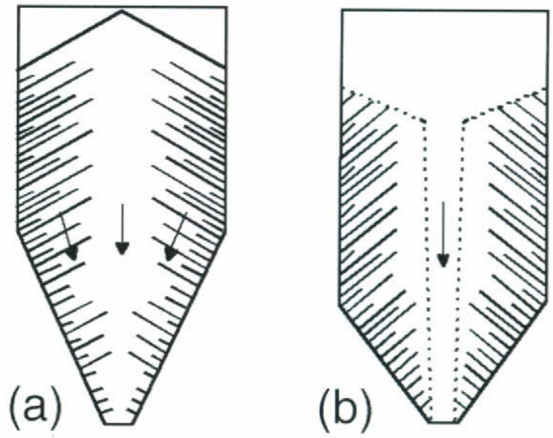


Figure 18. Scheme of bin discharge: (a) by mass flow (b) by funnel flow.

5.3 POLISHING DIFFICULTY

Porcelain tile polishing is an expensive process involving significant consumption of raw materials and energy. The difficulty of polishing porcelain tile has a double origin. On the one hand, porcelain tile is a very hard product, which requires the use of very hard conventional abrasives, such as silicon carbide, or even super-abrasives such as diamond. Figure 19 shows the position of porcelain tile in a diagram that attempts to symbolise the polishing difficulty. The diagram depicts, in qualitative form, the hardness and toughness of different materials, including porcelain tile. The polishing difficulty increases according to the diagonal of the two Cartesian axes, i.e., on increasing the hardness and toughness of the material to be polished. It can be observed that porcelain tile is a difficult material to machine.

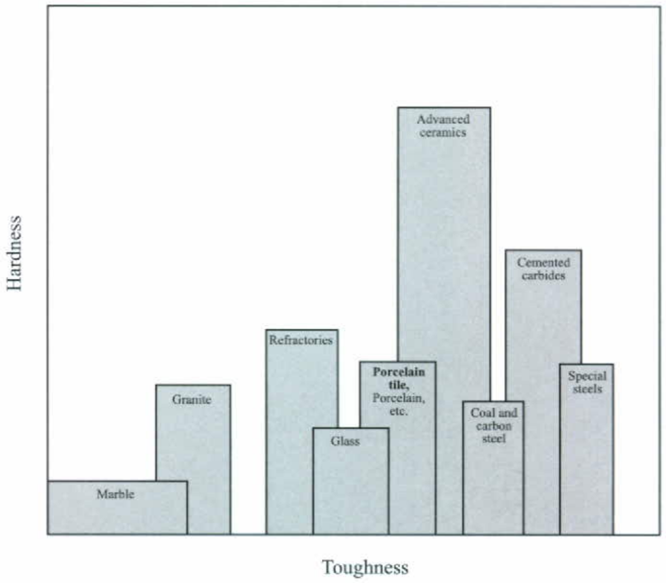
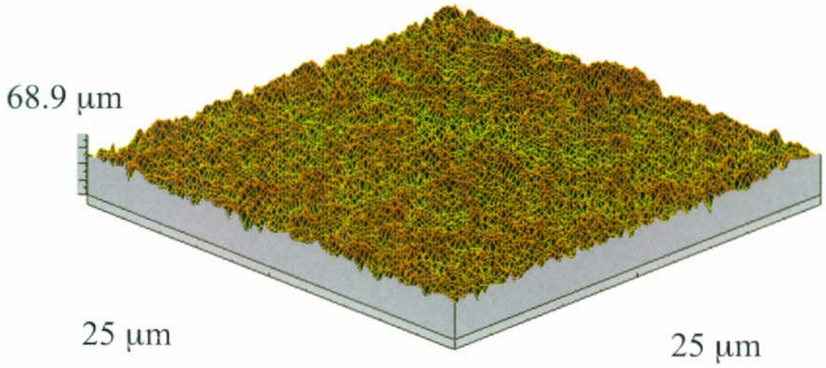


Figure 19. Diagram of polishing ease (hardness versus toughness). Polishing difficulty increases according to the diagonal of the co-ordinate axes (Source: ref. 35).

On the other hand, after firing the product is not flat, but rather presents various types of curvature, which enormously hinder the action of polishing tools. To facilitate this action, it is necessary to reduce tile curvature, using diamond tools that need to remove a great quantity of material, with high energy consumption, while also producing considerable deterioration of the tile surface (Figure 20). This deterioration conditions the rest of the polishing operation tremendously, since the damage suffered by the tile needs to be repaired by successive tools containing progressively smaller-size abrasive (silicon carbide) grit. As Figure 21 shows, around 70% of the industrial polishing train is used to repair the damage caused in the initial levelling step, which takes place with considerable material removal. After this step, gloss increases rapidly, tending finally to a more or less stable value, which as set out in the literature [36,37] is related to tile porosity.

Unpolished tile



Tile after levelling

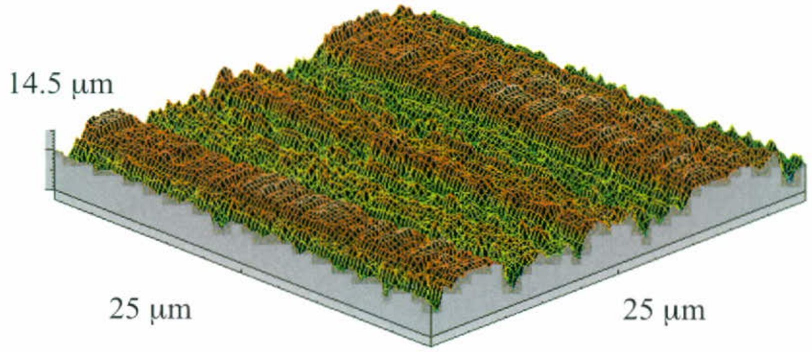


Figure 20. Appearance of the porcelain tile surface after the levelling step (comparison with the original surface).

The use of tools that deteriorate the tile surface less in the levelling step, and diamond tools that increase the effectiveness of the actual polishing step are two proposals currently already in an advanced state of development, which will lead to improved efficiency of the operation, reducing its ecological rucksack (consumption of raw materials and energy) and reducing the environmental impact.

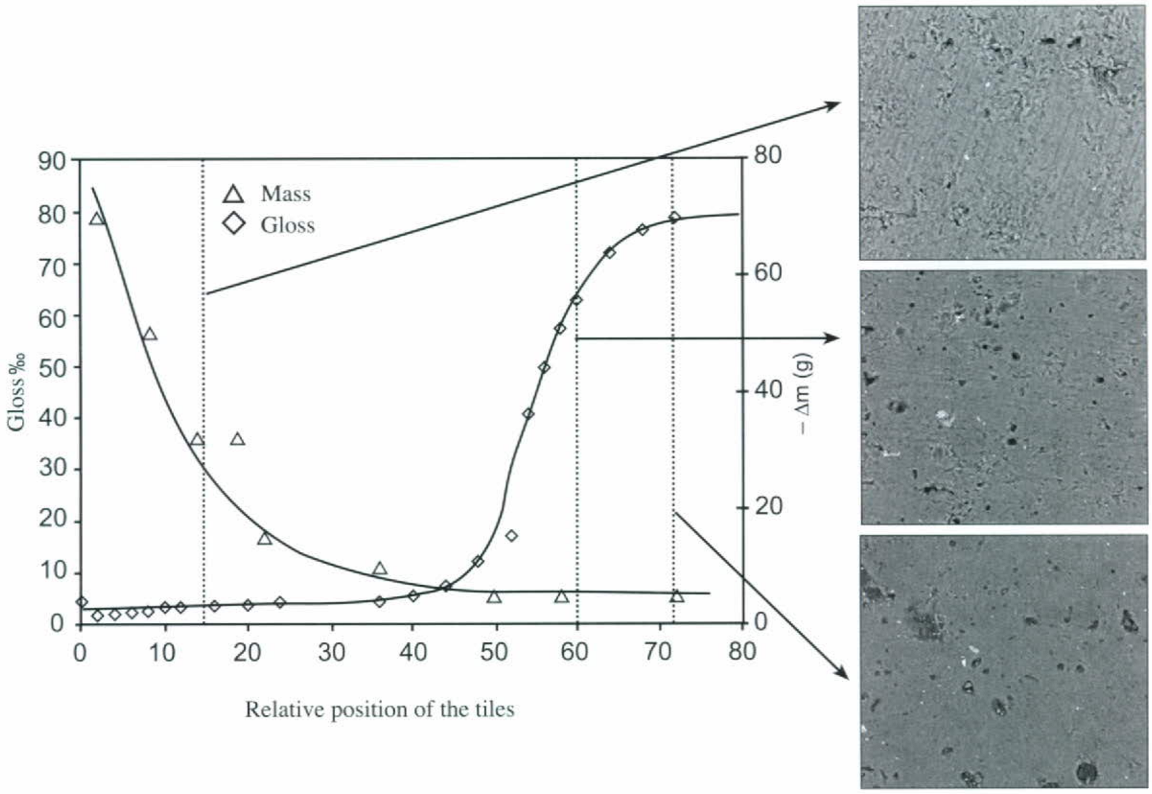
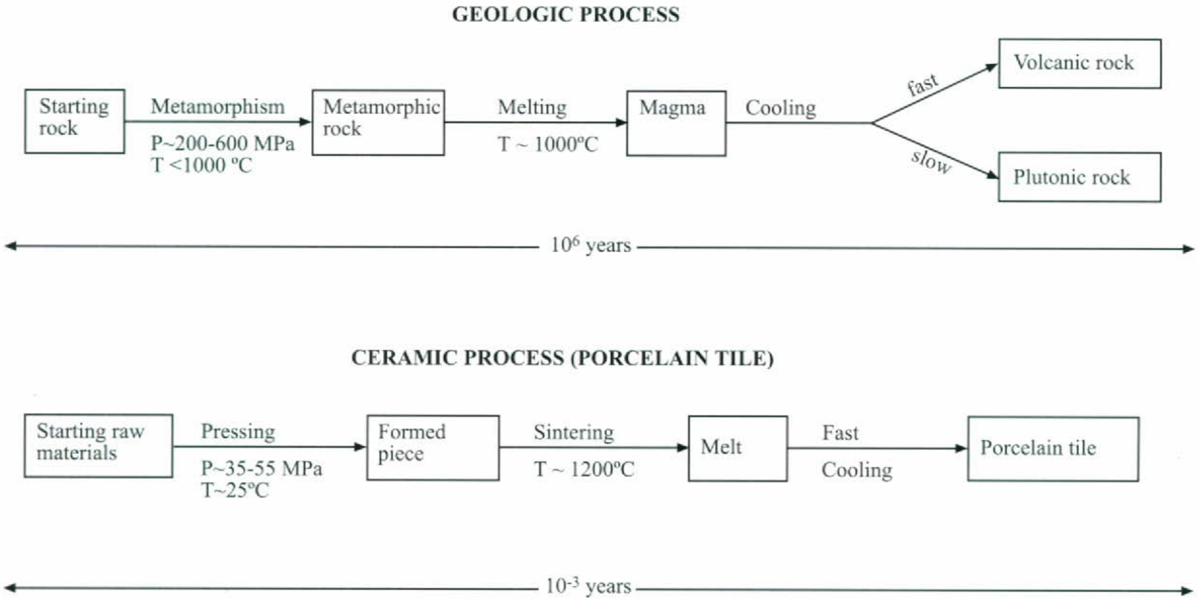


Figure 21. Variation of material loss and surface gloss during porcelain tile polishing.

6. PORCELAIN TILE AND NATURAL STONE: TWO SIDES OF THE SAME MATTER

The latest discussion forums on the future of porcelain tile [1,38] suggest that the immediate future of the product is a firmly associated with reproduction, not just of typically polished decorative stone such as granite and marble, but also of quarry stones such as sandstone, slates, etc. This has been showcased at the latest ceramic tile trade fairs, which are starting to resemble an exhibition of natural stones rather than a ceramic event. Some companies are making this tendency a marketing policy by omitting the word "ceramic" and all related terms in their advertising. This tendency is based on the possibility of reproducing a natural material, while improving its performance (reducing porosity and improving its mechanical strength, and resistance to stains and frost) at a highly competitive price, or achieving market growth by reproducing natural materials that are being depleted. The field moreover is simply huge, since over 5000 types of commercial natural stones are found worldwide, with innumerable stones not in the sales catalogues.

From a scientific point of view, the classification of natural stones encompasses the whole range of causal antecedents of the rocks, from those with an igneous origin such as granite, to a purely sedimentary origin such as limestone, via the typical metamorphism of slates [39], etc. Figure 22 presents a highly simplified vision of the causal genesis of natural stone, compared with the porcelain tile production process. It can be observed that both materials exhibit great similarities. However, there are also differentiating features: the time scale and the simultaneous application of pressure and temperature during rock genesis. This differentiation makes reproduction on an industrial scale of the effect achieved by the nature over millions of years, using different synthesis conditions, extremely difficult. Thus for example, the size of a crystal in a granite produced by cooling magma generally exceeds 5 mm and can even reach 1 cm. On the other hand, the application of high pressures (up to 700 MPa) and temperatures (up to 1000ºC), during geologic times favours producing mineralogical species or crystalline lattice modifications which are unthinkable under current industrial manufacturing conditions.


GEOLOGIC PROCESS

CERAMIC PROCESS (PORCELAIN TILE)

Figure 22. Comparison between the genesis of natural stone and the porcelain tile manufacturing process.

This new tendency, targeting more and better reproductions of natural stones, requires developing new research lines in porcelain tile, which to date have tended to focus more on product performance. This new driving force could be defined as porcelain tile aesthetic engineering, and should envisage actions in product design and manufacturing technology.

6.1 NEW LINES OF R+D+I IN MATERIALS ENGINEERING

To engineer materials for use in porcelain tile production, some future research lines could be:

- Rediscovery of phase diagrams. Phase diagrams were abandoned in designing porcelain tile compositions since they were practically wholly based on the porcelain composition, with minor modifications. This tool enables more rationally analysing the melting and crystallisation routes of starting compositions, in order to engineer new glass-ceramic materials or predict solid solution phenomena, exsolution or phase separation, which favour achieving certain aesthetic effects. In this respect it is convenient to note that the possibilities of using glass-ceramic materials are greater in the case of porcelain tile compared with the glaze coating, since the firing temperature is higher and the smooth glossy finishes are generally produced by mechanical procedures such as polishing.

- Granular and microgranular applications that encourage the imitation of crystalline growth, coloration, exsolution and other phenomena which take place during magma cooling in the genesis of the natural stone. This line of action would also be undertaken in relation with the engineering of materials of an essentially vitreous nature, which imitate the transparency of single crystals or large-size crystalline aggregates.

- Development of compositions with very high degrees of whiteness and optimum colour development

- Engineering of materials for application by non-contact decorating techniques, such as laser [40], inkjet printing [41], etc. Some of these materials could include nanoparticle suspensions, gels, ceramic-polymer composites, etc.

- Development of ceramic materials with very small particle sizes and high flowability for dry application. This will require exploring new powder fluidisation techniques such as those based on particle encapsulation and microencapsulation [42].

6.2 NEW R+D+I LINES IN MANUFACTURING TECHNOLOGY

The new tendency in aesthetic engineering indicated above will also require implementing new manufacturing technologies, which will need to be supported by extensive R+D+I work.

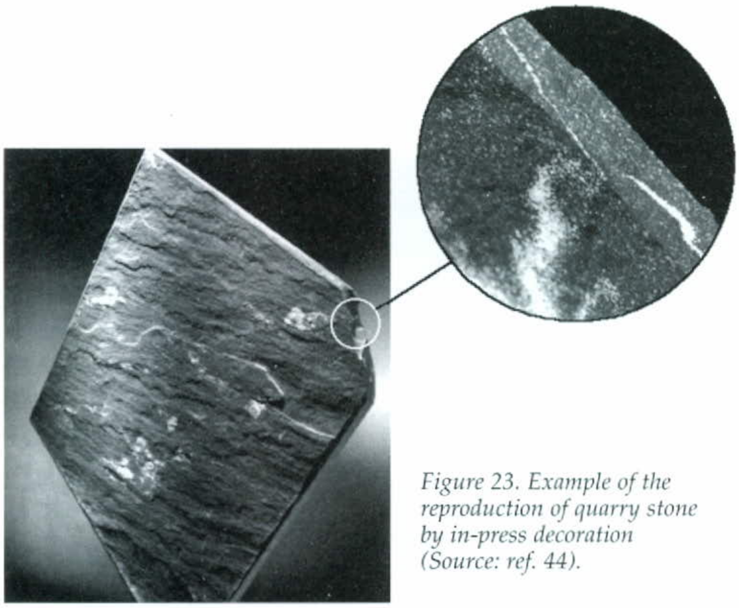


Figure 23. Example of the reproduction of quarry stone by in-press decoration (Source: ref. 44).

At present the gradual transfer of the decorating line from its traditional location after the dryer, to the pressing section is already a reality [43]. The driving force behind this change is the above-mentioned reproduction of stone effects, many of which lose their intensity and effectiveness when it is attempted to produce them in a traditional glazing line. The tile shown in Figure 23 exemplifies this. As can be observed, the depth of the veining or bas-relief decoration would be impossible to achieve by current glazing and decorating approaches (screen printing, rotogravure, etc).

Some of the future R+D+I lines relating to porcelain tile manufacturing technology focussing on the trend mentioned above could be:

- In-press tile decoration [43]. This course of action is already in a clear development phase, as indicated, and a growing evolution is expected in the future, by incorporating new decorating systems at the press. Of the latest systems (powder screen printing, pre-charge systems, multiple charging, material removal by pneumatic pressure, etc), it is perhaps the double-pressing technique that poses the greatest technological challenge. All these systems, as well as their combination and the new proposals that appear, will require considerable research efforts to improve an increasingly complicated and demanding pressing operation.

-Non-contact decorating systems. Bas-relief decoration could be the gateway for the incorporation of an infinity of decorating techniques requiring no contact with the substrate to be decorated, such as:

- Laser decoration. Laser technology, greatly developed in the last few years [40], could find an important field of application in porcelain tile, such as in producing reliefs, texture changes (matt-gloss effects), decorating on relief and bas-relief, tile cutting, sintering, polishing, etc.
- Inkjet printing. Ceramic inkjet printing has recently been developed [45] and is already in the industrial implementation phase. This technology has required and will in the future require even further adaptation of the solids used in the ink formulation, taking into account the emerging technology of nanoparticle synthesis. However, other inkjet decorating systems exist that could also be incorporated in the near future, such as those based on applying a binder to a bed of particles, or by injecting a gelling agent into a suspension layer [41].

-Mechanochemical polishing, widely used in other industrial sectors, could provide an important improvement in the surface finish of polished tiles [46].

-New tile forming methods:

- Hot pressing. Setting forth the transfer of the decoration line toward the press, in the future, we might be able not only to decorate but also to fire, i.e. to apply heat, in the press itself, as occurs in rock metamorphosis. With this technique, aesthetic effects could be achieved, at present unimaginable by the traditional process (cold pressing followed by sintering). This technology is widely used in producing advanced ceramics [47], and in sintering metals and glasses.
- Forming based on the melt. Given the glass-ceramic characteristic of the product, the possibility could be considered of manufacturing porcelain tile according to the technology used in the glass industry for producing glass-ceramic materials: forming of the melt, for instance as a sheet, followed by thermal treatment to produce the crystalline phases. This technique would hugely extend the glass-ceramic systems that could be used.
- Producing sheets. A recently presented innovation [48] related to porcelain tile is the production of thin sheets (up to 3 mm) to be marketed on a substrate that provides a certain rigidity. The porcelain tiles (sheets) are made by pressing the powder held between two flexible sheets at very high pressure. This innovation is directed toward new applications of porcelain tile, different from current ones, for replacing materials such as wood, plastic or metal, since the possibilities regarding the tile sizes that can be manufactured are practically unlimited. Following on with this new line of development, other sheet-forming methods could be incorporated into porcelain tile production technology, such as tape casting, typically used in producing electroceramics [49]. The advantage of this last technique is that the sheet is obtained directly from the suspension, without previous spray drying.

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