STUDY OF POROSITY IN PORCELAIN TILE BODIES

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1. INTRODUCTION

In all ceramic materials, and in particular in the ceramic floor and wall tiles, porosity has a considerable influence on the technical characteristics, mainly on mechanical characteristics (modulus of rupture) and surface characteristics (abrasion resistance, stain resistance, resistance to chemical agents). The low porosity of a fired piece is to a large extent responsible for the material's good mechanical and chemical properties, and enables using the product in outside environments. Therefore, with a view to reducing porosity in the finished product and to extending possible product applications, the ceramic industry has developed the technology for making porcelain floor tiles, whose water absorption is practically zero (< 0.1%). Thus, it can be said that in porcelain tile bodies, porosity is an undesirable result of the vitrification process of the ceramic body and adversely affects the physical and chemical properties of the ceramic material.

In a simplified way and as a generalisation it can be stated that porcelain tile bodies fundamentally display a triaxial formulation, based on three raw materials; clay minerals (illitic-kaolinitic clays and kaolins, like ball-type plastic clays) which contribute the necessary plasticity for forming in green state and assure the mechanical strength of the pieces in drying, a high content in sodium-potassium feldspars, which provide the first liquid phases that appear during firing, and are therefore the initial promoters of the densification process, which contributes most to reducing tile porosity, and finally, feldspathic or quartz sands, which are used for the physical and chemical fit of the body.

The objective of the present work has been to identify the different types of porosity and to associate these with each of the components in the bodies (clay minerals, feldspars and quartz or sands), then analysing the effects that each of the types of porosity present has on some physical properties (mechanical and chemical) of white porcelain tile bodies.

2. METHODOLOGY

Several industrial samples have been selected from the national white porcelain tile production sector, and the microstructure of different white porcelain tile bodies has been studied by scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM/EDX) with a LEO 440i instrument.

3. EXPERIMENTAL

The results obtained have allowed making a classification of pore types (figure 1) and their origin in stoneware and white porcelain tile bodies.

Thus, it has been possible to establish that apparent porosity is formed by intercommunicated irregular channels whose cross-section appear as small orifices of very irregular form, normally with a size below 5 µm. Their origin lies in the loss of volume in clay mineral dehydroxylation in firing. During the sintering process liquid phase develops and progressively closes the capillaries that form the apparent porosity, giving rise to small size closed pores distributed throughout the clayey matrix. This type of closed pore is known as fine closed porosity, with a more or less spherical morphology from the closing of the apparent porosity, which practically disappears entirely.

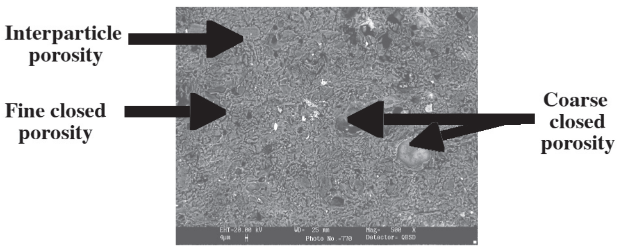
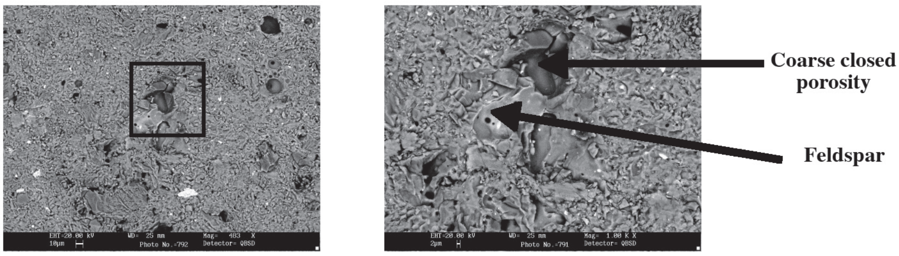


Figure 1. SEM Micrograph of a porcelain tile obtained at a magnification of 500x, in which the three types of porosity mentioned can be distinguished.

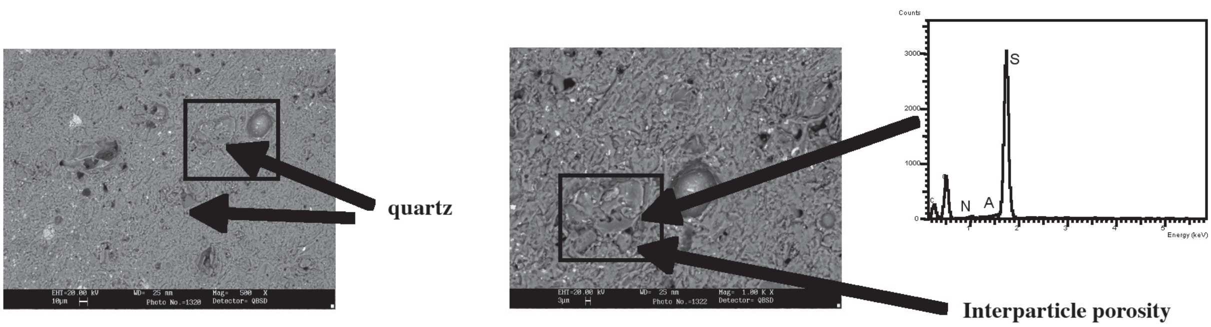
Spherical pores of intermediate size have also been found, which can stem from the coalescence of the residual fine porosity and of their increase in size due to expansion of the gases trapped inside these pores, favoured by the reduction in viscosity and surface tension of the fused phase at high temperatures.

On the other hand, a series of larger isolated pores is distinguished, with a spherical shape, whose size usually exceeds 10 μm, known as coarse closed porosity. This pore type is normally found in the regions that have been generated from the flux (feldspars) and is the cause of the greater or lesser stain resistance of technical or unglazed porcelain, since when the fired body is polished, the closed porosity is exposed in the surface and dirt can then lodge in these voids. Coarse closed porosity is mainly due to the decomposition of inclusions rich in volatiles from the feldspars and is directly linked to the fusion of the feldspar grains. The formation at low temperature of a fused phase with low viscosity from the flux facilitates pore expansion and the formation of spherical porosity of great size (figures 2 and 3).



Figures 2 and 3. SEM micrograph of a feldspar particle and the associated pore type, at magnifications of 500x and 1000x respectively.

Finally, the formation has been detected of pores with an irregular morphology at quartz and feldspar grain boundaries with the glassy matrix, which form so-called interparticle porosity (figures 4 and 5). These are responsible for the reduction in mechanical strength of the fired bodies, since they are considered stress concentrators and facilitate fracture. In addition, they encourage defects in the surfaces owing to the detachment of crystalline grains during the abrasion process that takes place in polishing and, consequently, also diminish stain resistance. Their origin lies in the presence of unmelted materials after firing and in the differences in the coefficients of thermal expansion of these residual grains with regard to the glassy matrix, so that during cooling the interfaces remain separate, giving rise to porosity that exists at ambient temperature (figure 6).



Figures 4 and 5. SEM micrographs of a quartz particle and a feldspar particle, together with their microanalysis at magnifications of 500x and 1000x respectively.

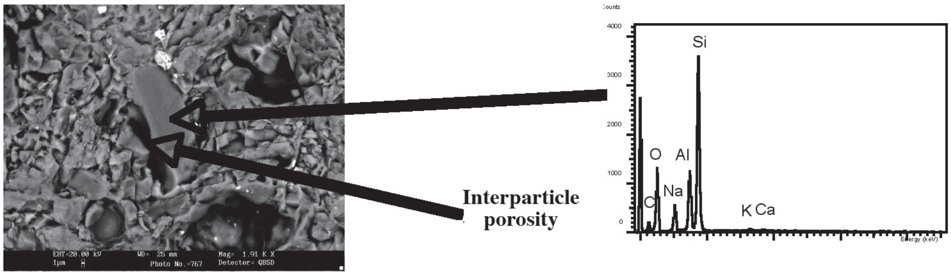


Figure 6. SEM micrograph of a feldspar particle at a magnification of 1900x together with energy-dispersive X-ray microanalysis (EDX).

4. CONCLUSIONS AND RECOMMENDATIONS

1) We can associate the different types of porosity to some of the raw materials that are used for the preparation of ceramic bodies. The following table summarises the results:

Type of porosity	Size	Raw material	Cause	Property
Open	< 5 µm	Clay minerals	Incomplete sintering	Frost resist.
Fine closed	Intermediate	Clay minerals	Lack of connectivity	--------
Coarse closed	> 10 µm	Natural fluxes (Feldspars, etc.)	Decomp. volatiles	Stain resist.
	> 10 µm	Fluxes	Low viscosities	Stain resist.
Interparticle		Quartz and feldspar	High expansion coef.	Mech. strength Stain resist.

2) Analyses have shown that coarse closed porosity and interparticle porosity are the major porosities. In order to improve the microstructure of porcelain tile bodies efforts need to focus on decreasing these, since they are responsible for the better or worse characteristics of the finished product. The minerals that generate these types of pores are the feldspars and quartz, and it will be necessary, therefore, to control well their physical, chemical and grain size characteristics or to seek other components that avoid or diminish the formation of porosity.

3) A possible solution would be to introduce a flux (wollastonite, high temperature frits, …) to react with the clayey components at lower temperature than the feldspars do, facilitating the closing of the fine residual closed porosity, and which would generate in addition a fused phase of high viscosity that avoided the increase in size of coarse closed porosity.

4) The impurities content involving volatile elements in the fluxing components must be the lowest possible to avoid formation of porosity in the melt that arises from the flux. In this sense, a synthetic and totally glassy product such as ceramic frits could be an interesting option.

5) The fluxes must be correctly milled, since the smaller the grain size and the larger the interparticle contact area, the greater will be the sintering in the solid phase, and the lower will be the working temperatures.

6) Another possible option for improving the characteristics of the body is to use non-plastics that do not consist of quartz, which would enable reducing interparticle porosity significantly. The ideal non-plastic would be a flux with low particle size, with optimum packing of the composition in the green state, and which gave rise to a melt at the lowest possible temperature with the maximum viscosity.

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