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PHYSICAL PORPERTIES OF PORCELAIN PREPARED USING ALGERIAN RAW MATERIALS

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ABSTRACT:

Porcelain is a type of ceramics highly valued for its beauty and strength. It is known primarily as a material for high-quality vases, tableware, figures and other decorative objects. Triaxial porcelain composed primarily of clay–quartz–feldspar is one of the most widely studied ceramic systems; it has got diverse applications like white ware, stoneware, insulators, etc. Extensive research on porcelain for a long time confirmed its complexities, so there remain significant challenges in understanding porcelain in relation to raw materials, processing science, phase and micro structural evolution. In the case of triaxial porcelains, the strength of the final product is the result of a complex interaction of a series of processing parameters such as the characteristics and composition of the starting materials, the conditions of mixing and forming, and the details of sintering, e.g. the furnace atmosphere and the ramp, soak temperature and duration of the heating cycle.

The fine porcelainized stoneware, more easily called porcelainized tiles, is a product having very good technical characteristics, as it shows a high flexural strength value.

In the ceramic tiles industry framework, the porcelainized tiles have become more and more important with regard to its spread from very few market shares limited as to their application fields to more and more diversified ones; the result has been a clear increase in production volumes.

This product, which was formerly considered from a technical standpoint, only, nowadays shows high aesthetical potentialities allowing its use for over-refined purposes. From a ceramic point of view, the porcelainized tiles are not a new product, as it comes from production technologies already used in the past which are now old fashioned; its present development is due to the introduction of proper and innovative chemical-mineralogical compositions, suitable for the application of modern technologies such as high pressure casting, new decoration techniques and, last but not least, fast firing even applied to big sizes.

This paper wants to offer a general approach to the market shares suitable for this product, to its technological aspects and processing phases, as well as to its future possible evolution.

To prepare porcelain, we have utilized raw Algerian materials and the mixture is consisting of 37% Kaolin, 35% Feldspar and 28% Quartz.

The mechanical properties of porcelain bodies have been studied extensively for almost a century. In addition to, the mechanical strength such as tensile and flexural strength is interesting porcelain characteristic. Specimen without calcinations and those calcined sintered at 1200°C for two hours with a treating rate of 5°C/mn, have tensile and flexural strength values of about 73 MPa and 196 MPa. The calcined and not calcined specimen flexural strength value is much higher than that of the strength conventional porcelain, which is of about 60.

The distribution of closed pores, their geometric shapes and possible link with each other control the flexural strength of the porcelain body. SEM examinations revealed the porosity developments therefore sets of SEM specimens without calcinations and those calcined sintered at 1200°C and 1250°C was examined.

Key words: *Porcelain; Kaolin; Quartz; Feldspath.*

INTRODUCTION:

Among ceramic tiles, porcelain stoneware is by far, the best product. Its very high density, due to selected raw materials used and the industrial fast firing cycles, confers to this class of products particular characteristics of mechanical strength and wear resistance[1-2]. This material is prevalently constituted by a glassy matrix in which bubbles of gas, developed during firing, are trapped and several crystalline phases, both residual crystals, such as quartz and feldspar, and new formed crystals, as mullite, are embedded [3]. These microstructural singularities inside a glassy matrix can lead to different toughening mechanisms. As regards, the quartz crystals can be responsible for different microcraking toughening mechanisms: (i) deflection of the crack trajectory, (ii) crack branching and sometimes, (iii) stopping of the crack [4-5]. In the toughening of the glassy matrix of porcelain stoneware material, the role both of the mullite content and the pores has been also considered [3]. On the basis of these observations, porcelain stoneware tiles, if compared with others typologies of products [6] present a relatively high value of fracture toughness, very close in any case to the value of glass, in agreement to the glassy nature of its matrix. However, even if it has to take into account for this significant difference, the high sensitivity of the material to the stresses coming from the environment, keeps on representing a serious drawback. Scratches, cuts and large areas, from which the material has been removed, still visible on the working surface of the tiles after the polishing operation, can be attributed both to a not correct machining procedure and parameters [7-8] and to the rather low fracture toughness, not sufficient to react to crack propagation. Although many efforts have been addressed to improve the mechanical strength of these materials, crack resistance has received, until now, little consideration.

Porcelain tiles were introduced at the end of 1980s by Fiandre, one of the leading Italian porcelain tile manufactures. Among the various types of ceramic floor and wall tile, porcelain tile is the product which is in recent years has shown the greatest rate of increase (on a percent basis) in the amount produced, amount sold, and obviously amount used. Actually the porcelainized tiles present the best technical characteristics, as it is a product basically composed of crystal phases at high hardness and sintered at a high temperature. One of its technical developments, meant to further increase its performance, may seem needless or not strictly necessary, from a commercial point of view. On the contrary, technically speaking, it must be pointed out a multiphased ceramic material shows an intrinsic microporosity, due to the inability of filling the empty spaces between the solid crystal particles and the surrounding glass phase, even after a long firing cycle. Of course, the porcelainized tiles are included in this group of materials but they show a minimum microporosity, which may cause a more or less remarkable tendency to the product dirtiness, if not properly controlled. In general, the values of open porosity are very low (about 0.1% as to the absorbed water and 0.5% according to the mercury porosimetry) and therefore the surface of the tile does not show any particular tendency to stains. Vice versa the internal closed porosity is around 6%, and the pore sizes range from 1 to 10µm; this porosity appears during the polishing phase where about 0.5÷1 mm of the superficial layer is removed. There are many ways of intervention (some of them have already been widely adopted) to reduce the effects or the incidence itself of the residual micro porosities on the product performance when used. On this, it has been shown the penetration of staining agents and their removal are connected with the pore size and diameter. Relatively big-sized open pores help an ease cleaning of the product, but they determine a visual decay of the surface. On the contrary, very small pores solve the problem before, as they prevent the interference of foreign substances; therefore, the latter case must be followed more and more to improve the product. Appropriate adjustments of the working parameters allow to highly increasing the degree of the material hardening, for example by:

- increasing the specific surface of the body components and acting on the grinding grade, particularly of the hard materials (quartz and feldspars);
- increasing the compactness of the powders by using high pressing pressures;
- using stronger melting agents.

Surely we will keep on using these and further solutions and we will get better and better results which will ensure a high standard quality of the porcelainized tiles produced in the next future.

RAW MATERIALS

The raw materials used for the body compositions of the porcelainized tiles can be divided into some groups of different minerals, each having its own function: the clayey raw materials give plasticity to the body, while the complementary non-plastic ones include melting minerals and the mainly leaning and structural ones. The clayey minerals of illitic-kaolinitic or montmorillonitic origin belong to the first group and show more or less remarkable plastic characteristics with regard to their mineralogical lattices and to their particle-size distributions. The melting minerals are feldspars and feldspathoids, talc, eurites, pegmatites, while quartz and generally quartzites are the most refractory ones of those having a structural function. A small amount of colouring oxides such as Fe2O3 and TiO2 is required to all components, so as to avoid the colouring pollution of the body natural colour. The quantities of the components depend on the mineralogical nature of the clays, on the clayey particle size distribution and finally on their reactivity to the melting minerals.

In order to choose the suitable raw materials, the properties of the final product had to be taken into consideration. A sufficient amount of feldspar is necessary to obtain the desired glassy phase. As in all traditional ceramics, the presence of quartz is necessary in order to decrease shrinkage. It also reduces the body tendency to warp or distort during firing. And Kaolin is characterized by low plasticity.

The major raw materials used in our study were collected from Algerian source (Kaolin was from Debagh deposit, Quartz from El Oued and Feldspar from Ain Barbar deposit).

Table1 gives the chemical composition by X-ray fluorescence of raw materials.

Table 1: *Chemical composition of the raw materials (weight %).*

Oxydes content	Kaolin	Feldspar	Quartz
SiO_2	37.77	60.68	86.68
Al_2O_3	35.50	10.68	0.91
Fe_2O_3	0.34	0.66	4.57
CaO	0.80	0.17	6.48
SO_3	0.95		
K_2O	0.28	>10.0	0.78
Cl	0.01		
MnO	0.89		0.09
TiO_2	0.06	0.11	0.12
Na_2O		0.48	

The relatively lower amount of Fe_2O_3 is an indication that the kaolin is adequate to the fabrication of ceramic products with lighter colour. The kaolin has also an amount of K_2O, which conveniently forms a liquid phase that contributes to densification at high temperatures. The amount of TiO_2 is considered normal but may cause a yellowish colour that is not satisfactory for white wares.

EXPERIMENTAL PROCEDURE

The porcelainized tiles are the development of the material called chemical stoneware, traditionally linked to small sizes and to the use of old-fashioned technologies. The newly-adopted compositions, the use of roller kilns and of modern hydraulic presses at high pressure and at precise pressing have allowed this product to be revised and its technological characteristics to be improved by applying the degree of reliability achieved by the fast firing.
The mixture consisting of 37% Kaolin, 35% Feldspar and 28% Quartz was mixed in alumina milling media and water for 5 h. The slurry was dried at 200°C for 2 h. A part of the powdered batches was calcined separately at 1000°C with a soaking period of 6 h. During the pressing phase, the target is to reach the highest degree of compactness for the dried powders before firing, consistent with the problems of degasification occurring in firing. The mixture was compacted into discs shape (13 mm x ~ 2 mm) by uniaxial pressing at 75 MPa. The over-compactness, the material is generally subjected to, gives rise to a strong hardening in the tile structure, which limits the shrinkage and greatly decreases the porosity of the fired product. Of course, the pressing specific pressure must be such that the particles thickening in the pressed tile allows the oxidation of the organic matters and the removal of the produced gases in firing. The specific pressure affects the absorption and shrinkage values of the fired tiles; high values of the pressed tile bulk density, and therefore relatively low shrinkages and surely lower porosity values, correspond to high pressing

pressures. Besides the pressing pressure, during the pressing phase the homogeneity of the powders loading inside the cavities of the presses is basic.

The firing cycle and temperature it is the final phase of the process, where the results of grinding and pressing come to light: the temperature and the cycle are the fundamental parameters to be carefully checked to achieve the fixed goal, that is the attainment of a vitrified material with a very low porosity.

Firing was carried out in a laboratory electric furnace reaching different maximum temperatures in the range 1125-1250°C with a soaking time of 120 min and heating rate of 5°C min^{-1}.

After firing, samples from porcelain tile polishing residue and from SiC abrasives were submitted to physical–chemical characterization. The tensile strength testing of sintered samples at room temperatures was carried out using the diametral compression test. Generally, three samples of each composition sintered under the same conditions were tested and an average value was taken. Following previous strength testing procedures, packing strips (Manila office file) of 0.30 mm thickness were used [9].

RESULTS AND DISCUSSIONS

The requisites for the finished product (nearly zero water absorption, very high values of flexural strength and resistance to deep abrasion, high resistance to stains) are affected by both the choice of the raw materials and the processing conditions during the basic phases of batching, grinding, pressing, drying and firing.

The samples were fired in the range 1125-1250°C. In consequence of firing, clays are subjected to top tactic reaction that destroys their structures. During the thermal treatment, clay react giving rise to endothermic dehydroxylation reactions. To higher temperature, from around 1000°C, the products of the dehydroxylation form different phases that culminate in the rapid crystallization of mullite. An amorphous phase is directly formed from the silica liberated during the metakaolin decomposition which is particularly reactive, possibly assisting the eutectic melt at 990°C with potash feldspar. This amorphous phase is responsible of the closing of the open pores, especially at the surface of the samples. Its amount and viscosity at the different temperatures is important together with the plateau time at the maximum temperature. Feldspars favour the fusion of some quartz in an amorphous phase. Over 1100°C, the mullite crystals are formed and absorbed into the matrix of silica and crystalline cristobalite. Very low porosity due to the glass phase is favoured by the fine size distribution of raw materials and a correct sintering cycle. It assures the high level of thermal shock resistance, abrasion resistance and cleanability. Regarding the raw materials used to produce ceramic bodies highly vitrified, feldspars develop an important role in porcelain tile pastes. In fact, the great densification and high mechanical resistance showed by these ceramic materials after firing are due the action of feldspars. Feldspars are largely used in ceramic materials with high densification like porcelain tiles, vitreous china, porcelains and semi-gres tiles [10].

The influence of starting composition on flexural strength of porcelain bodies have been experimentally studied by many researchers, because of its economic importance in ceramic industry. It is known fact that quartz grains in different sizes have significant effects on mechanical strength of porcelain bodies. Especially, it is proposed that flexural strength of the porcelains increases with an increase in inter planar spacing of quartz crystals, so the quartz is under the tensile stress, and consequently, the glassy matrix surrounding the quartz grains is a compressive stress which acts as pre-stress, improving mechanical strengthening. The pre-stressing effect due to the residual compressive stress at the glassy phase around the grain is large, which is related to the quartz grain size and the firing temperature [11]. Internal stresses arise, first, because of the difference in thermal linear expansion coefficients of α quartz and the glassy phase and, second, because of polymorphic transformation in silica. These stresses can be reduced substantially by decreasing dispersity of the initial and residual quartz. On the other hand, quartz makes up part of the crystalline phases of porcelain that impart the needed mechanical strength to engineering components. The more so, a considerable part of quartz passes into molten feldspar, which increases the strength of the glassy phase. A similar conclusion had been also reached that the mechanical strength of porcelain is influenced mainly by stresses set up in the glassy matrix rather than by the amount or size of mullite crystals formed [12]. This concept should be examined in detail in the future studies.

The flexural strength of porcelain bodies were measured as function of temperature T. This situation is illustrated in Table 2.

Table 2: *the mechanical strength of the dried samples.*

Samples calcined			
Temperatures °C	1125°C	1200°C	1250
Tensile strength (MPa)	18	45	24
Flexural strength (MPa)	49	122	65
Samples without calcination			
Temperatures °C	1125°C	1200°C	1250
Tensile strength (MPa)	43	73	49
Flexural strength (MPa)	116	197	122

The flexural strength behaviours of calcined porcelain bodies and those without calcination are not different. The flexural strength bodies without calcinations are higher than the others. It is obvious that these changes in flexural strength are related to total porosity developments in bodies. The modified formulations generally present, in calcination, a slight decrease in flexural strength that could have affected the brittleness of the calcined specimens.

The flexural strength of porcelain bodies increased with an increase in firing temperature and reached maximum values of about 122 MPa at 1200 °C for calcined samples and 197 MPa for samples without calcination. Theoretically, a maximum flexural strength developed when the apparent porosity decreased to zero (Fig. 4). After continuing the heating, the flexural strength values decreased with both corresponding microstructural changes, mainly caused by porosity developments, as examined in SEM studies (Fig.3). As a general rule, at the higher firing temperature, the higher flexural strength should be attained. However, after reaching the maximum temperature, the flexural strength begins to decrease due to closed porosity development. The mechanical strength is strongly dependent on the microstructure, especially on defects such as pores and cracks.

The flexural resistance of porcelain tiles is strictly correlated with the porosity of the material. In general, products with a high flexural resistance present a very compact texture, a smooth surface with low porosity and almost some coarse pores. On the contrary, surface with a wide range of pore sizes, in particular coarse and spherical, show the lower performances. Generally, porosity affects the mechanical property of ceramic materials in two ways: Firstly, it reduces the effective cross-sectional (load-bearing) area such that the mechanical property will be dependent on the minimum contact-solid area. The minimum solid (load-bearing) area is the actual sintered or the bond area between particles in the case of stacked particles, and it is the minimum web cross-sectional area between pores in the case of stacked bubbles. Secondly, porosity leads to stress inhomogeneities (stress concentrations) near the pores such that under mechanical loading, the true stress in the material is higher near the pores than at a far distance from them [12].

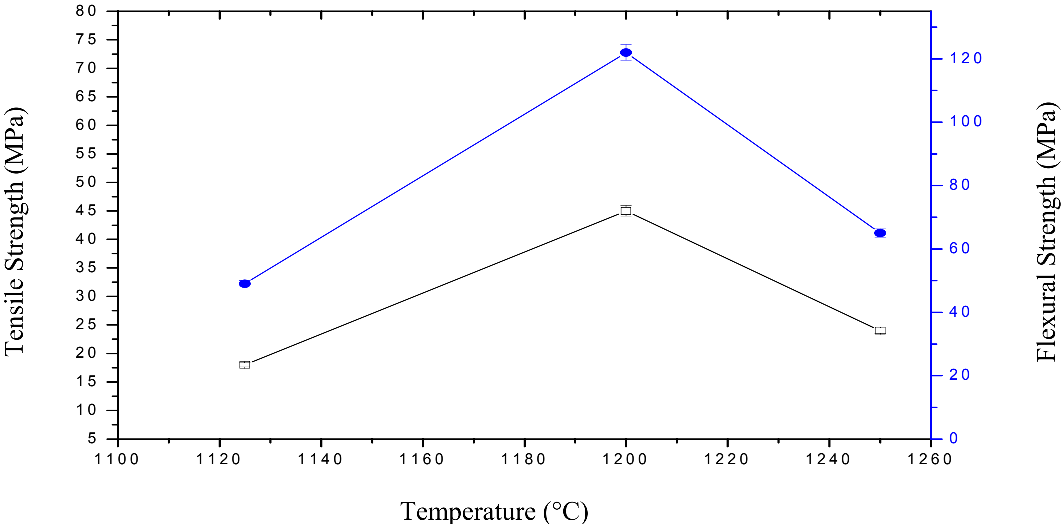

Figure 1: *Tensile and flexural strength as function of sintering temperature for calcined porcelain samples*

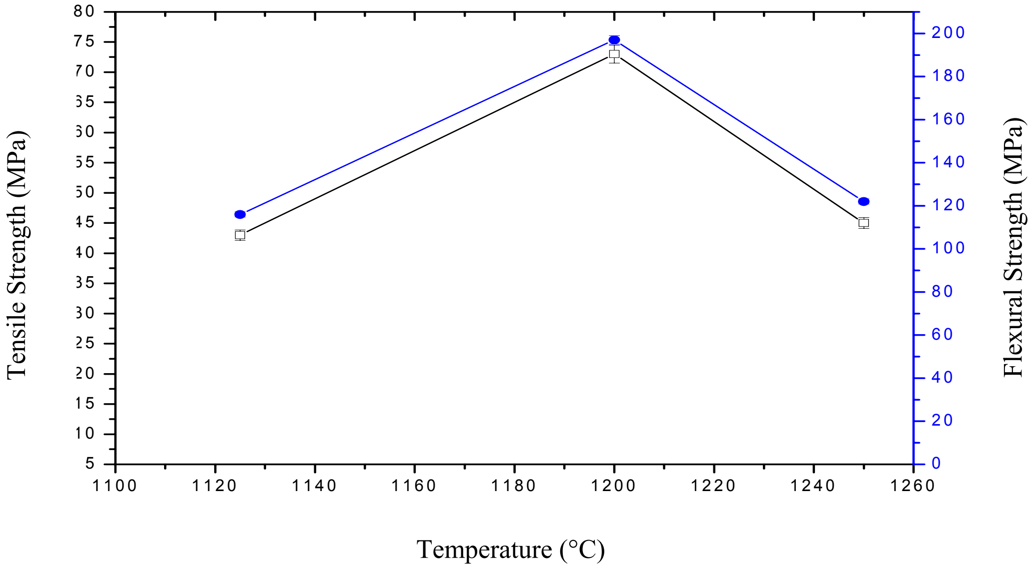

Figure 2: *Tensile and flexural strength as function of sintering temperature for porcelain samples without calcination*

The surface of porcelain tiles presents diverse microstructural elements, either intrinsic features [illegible] during the grinding [illegible] [14]:

(a) small sized (commonly <10μm), spherical pores, that were probably gas filled, so resulting insinterable during the industrial firing.

(b) coarse-sized (often >20 μm), irregularly shaped pores, presumably originated from coalescence of smaller pores during sintering or inherited by large defects of the green compact.

(c) Discontinuities around bigger particles, partly deriving from residual stresses (e.g. polymorph transition of quartz).

The surface morphologies of fired specimens without calcinations are carefully examined using broken fresh polished+etched surfaces by SEM techniques.

At 1200°C, porous structure was observed (Fig.4) in corresponding with SEM micrograph. The first possible reason for the formation of structure might be due to entrapment of vapour derived from the volatilization. The second possible reason might be due to the decomposition of any thermally unstable material and / or the water vapour present in raw materials. The derived vapour partially trapped by viscous body may cause the formation of pores.

SEM analysis of fracture surfaces reveals the presence of very narrow pores, most of which in round forms (Fig.4). The pores are small, closed and rounded, what can explain the good mechanical strength besides the very low porosity observed (Fig.3). It seems the product can present good thermal and acoustic insulation, but these properties were not analysed in this study.

SEM examinations revealed that the number of pores diminished and the size of pores increased at elevated temperatures (Fig.3). The shape of pores changed from irregular elongated shape to more spherical and ellipsoidal shapes at 1200°C (Fig.4). The shape, size and linkage trend of pores with each other played an important role in the flexural strength. These irregular shaped elongated pores decrease the flexural strength, in contrast, spherical pores formed after melting of quartz, show relatively higher strength. Kobayashi et al. [15]

also noticed changes in shape and size of pores with elevated temperature, and between the core and rim of porcelain. At high temperatures, feldspar grains are completely melted and spherical shape closed porosity increased clearly because of bloating pores (Figs. 3). Above this temperature, flexural strength decreased abruptly (Fig. 1, 2) and it decreased abruptly with increasing in pore sizes and porosity due to enhancing of the bloating effect (Fig.3).

It is therefore still valid to state that the results of image analysis indicate that the porosity and pore morphology (Fig. 3, 4), i.e. pore size and roundness/ sphericity, are all positive functions of sintering temperature. The roundness of the pores improved with temperature since the viscosity of the bodies was low enough for near spherical gas bubbles to form and retain their shapes.

The technical characteristics and, in particular, mechanical strength of porcelain tiles are strictly correlated with the porosity of material [16-17].

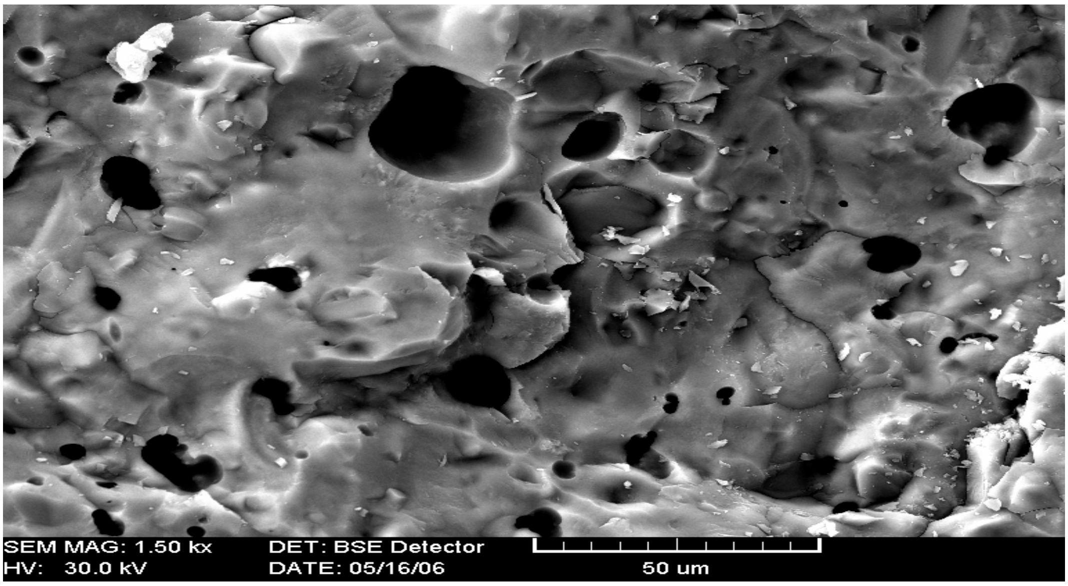

Figure 3 SEM *Micrograph of sintered specimen fired at 1250°C*

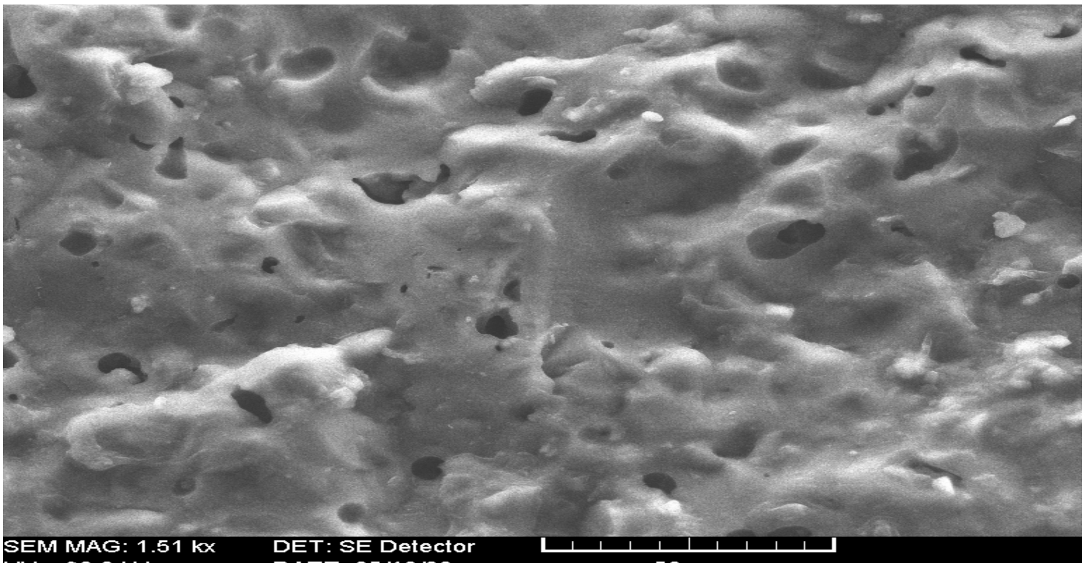

Figure 4 SEM *Micrograph of sintered specimen fired at 1200°C*

CONCLUSION

Actually the porcelainized tiles present the best technical characteristics, as it is a product basically composed of crystal phases at high hardness and sintered at a high temperature. One of its technical developments, meant to further increase its performance, may seem needless or not strictly necessary, from a commercial point of view. On the contrary, technically speaking, it must be pointed out a multiphased ceramic material shows an intrinsic microporosity, due to the inability of filling the empty spaces between the solid crystal particles and the surrounding glass phase, even after a long firing cycle. Of course, the porcelainized tiles are included in this group of materials but they show a minimum microporosity, which may cause a more or less remarkable tendency to the product dirtiness, if not properly controlled. In general, the values of open porosity are very low (about 0.1% as to the absorbed water and 0.5% according to the mercury porosimetry) and therefore the surface of the tile does not show any particular tendency to stains.

In our study, the mechanical resistance is due the rounded form of the pores present in the samples redistributing the tensions applied on the product, avoiding its concentration. It was observed good flexural resistance (average of 197MPa) which is much higher than that of the strength conventional porcelain which is of about 60 MPa and normally does not exceed 80 MPa, .showing that the product could be used as a building material for example. SEM studies revealed that small spherical shaped pores are the effects of bloating and more irregular shape, size and sharp edges of pores are due to melting effects. The pores are small, closed and rounded, what can explain the good mechanical resistance besides the very low porosity observed for these products. Closed porosity was minimised for temperature around 1200°C and increased above this temperature in accordance with a typical liquid phase sintering mechanism. It seems the product can present good thermal and acoustic insulation, but these properties were not analyzed in this study.

REFERENCES

1. Timellini, G. and Palmonari, C., Ceramic tile in urban design— application manual. Edi. Cer SpA, Sassuolo, MO, Italy, 2002.

2. Shanchez, E., Technical considerations on porcelain tile products and their manufacturing process. Interceramic, 52(1), 2003, pp. 6–16.
3. Souza, G. P., Rambaldi, E., Tucci, A., Esposito, L. and Lee, W. E., Microstructural variations in porcelain stoneware tiles as a function of flux system. J. Am. Ceram. Soc., 87(10), 2004, pp.1959–1966.
4. Leonelli, C., Bondioli, F., Veronesi, P., Romagnoli, M., Manfredini, T., Pellacani, G. C. et al., Enhancing the mechanical properties of porcelain stoneware tiles: a microstructural approach. J. Eur. Ceram. Soc., 21, 2001, pp. 785–793.
5. Valentini, M., Bigoni, D., Esposito, L. and Movchan, A. B., Crack deflection in ceramic materials. In Lecture notes, ed. D. Bigoni. Institute of Fundamental Technological Research, Warszawa, 2002, Chapter 3, pp. 43–56.
6. Esposito, L., Timellini, G. and Tucci, A., Fracture toughness of traditional ceramic materials: a first approach. In Proceedings of the 4th European Ceramic Society Conference, Vol. 1, ed. C. Palmonari, 1995, pp. 555–565.
7. Tucci, A. and Esposito, L., Polishing of porcelain stoneware tiles: surface aspects. In Proceedings of Qualicer, P.GI ,2000 , pp. 127–136.
8. Esposito, L., Tucci, A. and Naldi, D., The reliability of polished porcelain stoneware tiles. J. Eur. Ceram. Soc., 25, 2005, pp. 1487–1498.
9. Harabi A., Studies of an alumina-chromia system containing mullite. PhD thesis, Manchester Materials Science Centre, UMIST, Manchester, UK, 1990
10. Adriano Michael Bernardin , Darlei Souza de Medeiros , Humberto Gracher Riella, Pyroplasticity in porcelain tiles, Materials Science and Engineering A 427 ,2006, pp. 316–319
11. Isik Ece O., Zenbe-e Nakagawa, Bending strength of porcelains, Ceramics International 28, 2002, pp. 131–140
12. Andreeva N. A and Ordan'yan S. S., Technological implications in increasing the strength of porcelain , Refractories and Industrial Ceramics, 2002, Vol. 43, Nos. 11 – 12, pp. 325-328
13.Nyongesa, F.W. and Aduda, B.O.,Fracture strength of porous ceramics stress, concentration vs minimum solid area models, African Journal of Science and Technology (AJST) Science and Engineering Serie, 2004, Vol. 5, No. 2, pp. 19-27
14. Dondi M.,, Ercolani G., Guarini G., Melandri C., Raimondoa M., Rocha E.e Almendra, Tenorio Cavalcante P. M., The role of surface microstructure on the resistance to stains of porcelain stoneware tiles, Journal of the European Ceramic Society 25, 2005, pp. 357–365
15. Kobayashi Y., Ohira O., Ohashi Y., Kato E., Effect of Firing Temperature on Bending Strength of Porcelains for Tableware, J. Am. Ceram. Soc. 75, 1992, pp. 1801–1806.
16. Dondi M .et.all, The role of surface microstructure on the resistance to stains of porcelain stoneware tiles, Journal of the European Ceramic Society 25 ,2005, pp. 357–365
17. Sáncheza E., Ibáñeza M.J., García-Tena J., M Porcelain tile microstructure: Implications for polished tile properties, Journal of the European Ceramic Society, 26 (13), 2006, pp.2533-2540