MEXICAN PORCELAIN LARGE FORMAT GAUGED TILES: TECHNOLOGY VS NATURE

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RESUMEN

Porcelain ceramic tile is a product with optimal technical characteristics, since it exhibits high mechanical resistance values and, on the other hand, presents extremely reduced water absorption values, often below 0.1%.

In the context of the modern tile industry, porcelain ceramic tile has been growing in importance with its diffusion from very specialized market segments, to a broader spectrum of application. This has led to a visible increase in production volume. This

product, appreciated in the past only for its technical specifications, is currently characterized by a remarkable aesthetic potential which allows its penetration toward more sophisticated uses.

In fact, porcelain tile is the ceramic tile that presents the best technical characteristics, it being a product made primarily of crystalline phases of high hardness, sintered at high temperature. Thus, its evolution, taking into account the current production trends, inevitably leads to suppose that this product will go the already undertaken way of the expansion of the range of decorative effects, which have contributed so much to its diffusion. This aesthetic evolution, which is already a reality, can only increase the added value of the product, further promoting its dissemination in segments of the market increasingly oriented to residential use, and the external cladding of buildings with "pieces" of large format, 100 x 200 cm or more.

This research includes the results of tests conducted with standard methods on 24 "ultrathin" or "gauged" porcelain ceramic tile prototypes, developed from Mexican raw materials, to demonstrate that the production of this new type of product is possible in this country. Since Mexico does not currently have the necessary technology for the manufacture of slabs of large format and nominal thickness of less than 6.5 mm, different mixtures of raw materials were sent to two of the main producers of this type of tile, Sacmi in Bologna, and System Ceramics in Modena, in the heart of the Italian ceramic district, where 90% of the development and innovation of the ceramic industry in Italy is concentrated. One of the objectives of the project was the development of a Mexican standard to ensure the quality of the ultra-thin slabs; however, to verify the performance of quality from the ultra-slim tile, it was necessary to test rupture modulus, breaking strength and water absorption values for the developed prototypes.

The obtained results showed that it is possible to produce "gauged" or "ultra-thin" porcelain ceramic tiles of large format, with the raw materials that the Mexican industry is currently using, with the adoption of the newest pressing technology.

1. INTRODUCTION

The manufacture of ceramic tiles and floorings is an activity that has been conducted for more than 2000 years through the evolution of the different civilizations and cultures that have populated our planet. Since Man discovered the effect that heat generated on clay mixtures, turning them into articles of stone consistency that could be used to cover the soils of tamped earth, an activity began that today represents one of the most important industrial sectors in the field of construction and for the comfort and quality of life of consumers worldwide.

From the first clay floors to the modern tiles manufactured today, the ceramic coverings industry has developed a series of technological advances, based on the composition of raw material mixtures and a better energy efficiency, which have led to the emergence in the market of products whose characteristics and properties make them superior in many ways to other materials used for covering floors and walls, such as wood, stone, carpets or linoleum.

Within the global scene, Mexico ranks eighth globally in the production of ceramic tiles. In this sense, the development of new products has become a priority interest for ceramic tile companies. In the last two decades the development of a new type of ceramic covering called "porcelain" was achieved due to the chemical composition of the clays used for its manufacture, which is very similar to porcelain. These products are characterized by very low water absorption, due to their low or no porosity, which in turn give them mechanical properties far superior to those achieved by tiles made of traditional clays.

From a ceramic point of view, porcelain tile is not a new product, since its origin dates back to productive technologies already in use in the past and today surpassed; its current development must be associated with the introduction of appropriate innovative chemical-mineralogical compositions, in accordance with the application of modern technologies such as high-pressure forming, recent decoration techniques and the dissemination of fast firing for large formats.

In fact, porcelain tile is the ceramic tile that has the best technical characteristics, it being a product consisting mainly of crystalline phases of high hardness, sintered at high temperature. Thus, its evolution, taking into account the current productive trends, inevitably leads to the assumption that this product will follow the path already undertaken of the extension of the range of decorative effects, which have contributed so much to its dissemination.

This aesthetic evolution, which is already a reality, can only increase the added value of the product, further promoting its dissemination in market segments increasingly oriented to residential use, and to the external cladding of buildings with "pieces" of great format, even 100 x 200 cm or more.

One of the objectives of this work was to establish the feasibility of producing porcelain ceramic tiles from Mexican raw materials, by testing samples from the different clays used by the national ceramic sector for the generation of common ceramic tiles and determining whether these are suitable for the generation of the aforementioned products.

As can be seen in Figure 1, it was established with the industrial sector that the clays from companies marked in Figure 1 presented the best possibilities to meet the necessary requirements for the production of ceramic tiles of the porcelain type, which are characterized in the first instance by having water absorption values below 0.5%

after firing, mainly due to their high density and almost total absence of porosity. Also included in the study were 2 imported clays, as reference, since these have already proven to be suitable for the production of porcelain tiles. Figure 1 shows the geographical distribution of the national clays used in this project, as well as the two reference clays.

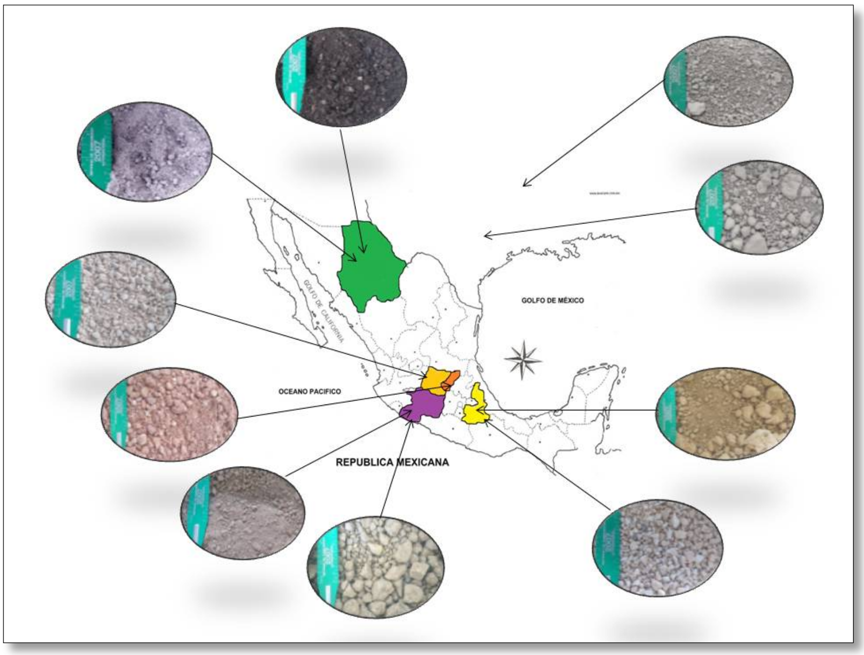

Figure 1. *Geographical distribution of different Mexican and imported clays for porcelain tile production.*

Clay	Density (g/cm^3)	Milling	Mineral Phases	Firing colour	Softening temp. (°C)	Z Potential (mV)	
						Deflocculant	No deflocculant
Chihuahua A	2.54	97%	Kaolinite, Illite, Orthoclase, Quartz, Tridymite, Cristobalite Anorthite	Light Gray	1320-1350	23	27
Chihuahua B	2.57	87%	Kaolinite, Quartz, Tridymite, Cristobalite	Gray	> 1490	11	20
Guanajuato	2.36	75%	Kaolinite, Quartz, Tridymite, Cristobalite	White	1490	13	21
Michoacán A	2.35	87%	Kaolinite, Quartz, Tridymite, Cristobalite Anorthite Muscovite	Dark brown	1490	19	32
Michoacán B	2.30	88%	Kaolinite, Quartz, Tridymite, Cristobalite, Muscovite	Dark brown	> 1490	16	23
Puebla A	2.45	63%	Kaolinite, Illite, Orthoclase, Quartz, Tridymite, Cristobalite Anorthite Muscovite	White	1340-1380	15	23
Puebla B	2.53	95%	Kaolinite, Quartz, Tridymite, Cristobalite, Muscovite	Brown	1490	15	34
Querétaro	2.57	68%	Kaolinite, Quartz, Tridymite, Cristobalite	White	1490	16	26

Table 1. *Composition and properties of Mexican clays.*

Table 1 shows primary characterization values of Mexican clays used for producing porcelain ceramic tiles.

2. JUSTIFICATION

For the application of exterior coverings on buildings, it has been considered that the normal thickness of the tiles (about 10 mm) makes them too heavy, and therefore poses a risk, when placed on the exterior facades of buildings at great height. An alternative solution has been proposed for several years with the development of ultra-thin tiles, with nominal thicknesses less than 6.5 mm and reaching minimums of 3 mm, without prejudice to most of the technical characteristics of the porcelain family. In fact, it has been shown that these products have the same values for almost all properties that normal thickness tiles exhibit, with the exception of the so-called "breakage resistance" or "breaking strength", whose value is diminished as a direct consequence of the reduction in thickness, which makes the piece less resistant when subjected to facial load. This report includes the results of tests performed with standard methods on 24 prototypes of "ultra-thin" porcelain ceramic tiles, developed from Mexican raw materials, to demonstrate that the production of this new product typology is possible in our country. Since Mexico does not currently have the necessary technology for the manufacture of large-format slabs with a nominal thickness of less than 6.5 mm, different mixtures of raw material were sent to two of the main producers of this type of tiles, Sacmi in Bologna, and System Ceramics in Modena, both in the heart of the Italian ceramic district, where 90% of the development and innovation of Italy's ceramic industry is concentrated.

3. METHODOLOGY

Since the properties of ultra-thin porcelain tiles have been shown to have the same values as normal thickness porcelain tiles, with the exception of breakage resistance, this study focused on the determination of 3 main parameters: a) the water absorption percentage, b) the rupture modulus (MOR), and c) rupture resistance or "breaking strength".

3.1. WATER ABSORPTION TEST

For the determination of the water absorption percentage of the developed prototypes, two standard test methods contained in ASTM Standard C373-2016 were used: a) water absorption percentage determined by the boiling impregnation method, using a 20 l stainless steel pan, and b) water absorption percentage determined by the vacuum impregnation method, using an ISOVACUUM 200-CC (Gabbrielli Technology).

3.2. MODULUS OF RUPTURE

The modulus of rupture, expressed in N/mm^2 is the value that is obtained by dividing the calculated fracture resistance, by the square of the minimum thickness of the breakout axis. The standard test method is contained in ASTM Standard C674-13. It is generated by applying a force at a certain speed on the center of the tile, with the appropriate point of application being in contact with the tile surface.

For this purpose, two parallel cylindrical supports are used on which the sample is placed, while a third cylinder, also parallel to the two above, rests on the upper face of the tile, at the center of the tile and an equidistant separation with each of the cylindrical supports. Force is applied at a constant increment rate, until the piece fails by fragile rupture. The determination of the breakout modulus (R) is done according to the formula:

$$R = \frac{3Fl_2}{2bh^2}$$

Where R is the rupture modulus expressed in N/mm2, F is the load force in N, l_2 is the spacing between the two support rollers, b is the width of the piece in mm, h is the minimum thickness through the breaking axis.

3.3. BREAKING STRENGTH

This method of testing consists of supporting the sample of the tile on the end of three cylindrical posts, or three steel balls, in an equilateral triangle arrangement, and applying a force to it at a rate defined in the center of the sample, which matches the center of these triangular supports, until the piece breaks.

Thus, the test provides a means to establish whether a ceramic tile meets the resistance requirements that have been specified for it. The resistance of the tile is the force, in lbf or N, read from the load cell, necessary for the tile to break. The method specifications are contained in ASTM C648-2009.

An INSTRON Model 59450 universal test machine with a maximum load capacity of 250kN was used for both Rupture Modulus and Rupture Resistance tests, with accessories manufactured specifically for each test.

3.4. PROTOTYPES OF ULTRA-THIN PORCELAIN TILES

Table 2 shows the compositions of the mixtures that were sent to Italy, for the manufacture of the prototypes.

Raw Material	Country of origin	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
Feldspar	Mexico	40 – 60%	40 – 50%	40 – 50%	20 – 30%	25 – 35%	40 – 50%
Kaolin	Mexico	20 – 35%	15 – 25%	20 – 30%	40 – 50%	40 – 50%	25 – 35%
Plastic Clay	Mexico	20 – 35%	10 – 20%	-	-	-	-
Plastic Clay	United States	-	10 – 20%	20 – 30%	20 – 30%	25 – 35%	25 – 35%

Table 2. *Composition of different 7imple mixtures used to produce large format prototype tiles*

4. RESULTS AND DISCUSSION

4.1. WATER ABSORPTION

Since two different methods were used, the results of the water absorption tests presented below in the following figures come from the average value obtained for each specimen when tested with the two techniques, though it is not intended to determine differences between methods but to specify the classification of the prototypes analyzed.

From the above results it can be established that the chemical composition of the mixture used influences the final densification achieved during sintering, as can be seen in Figure 3, since, as a greater amount of Mexican clay is replaced by imported clay, water absorption values are reduced to the specification range for porcelain tiles, while mixtures generated with 100% Mexican raw materials remained within the classification for ceramic stoneware tiles.

Figure 4 present the average values of water absorption test results, by boiling and vacuum methods, for prototype tiles of 5 and 6 mm rated thickness. In these, it may be observed that, when the thickness increases, the absorption values tend to regularize, although the tendency of ceramic stoneware classification is preserved for those tiles of Mexican clay content greater than 20% by weight.

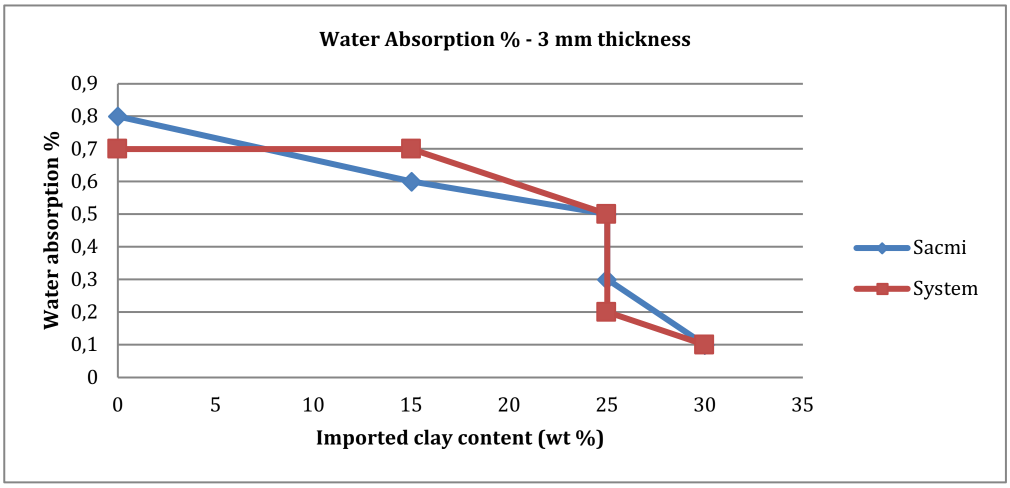

Figure 3. *Effect of imported clay content on water absorption for 3 mm thickness prototypes.*

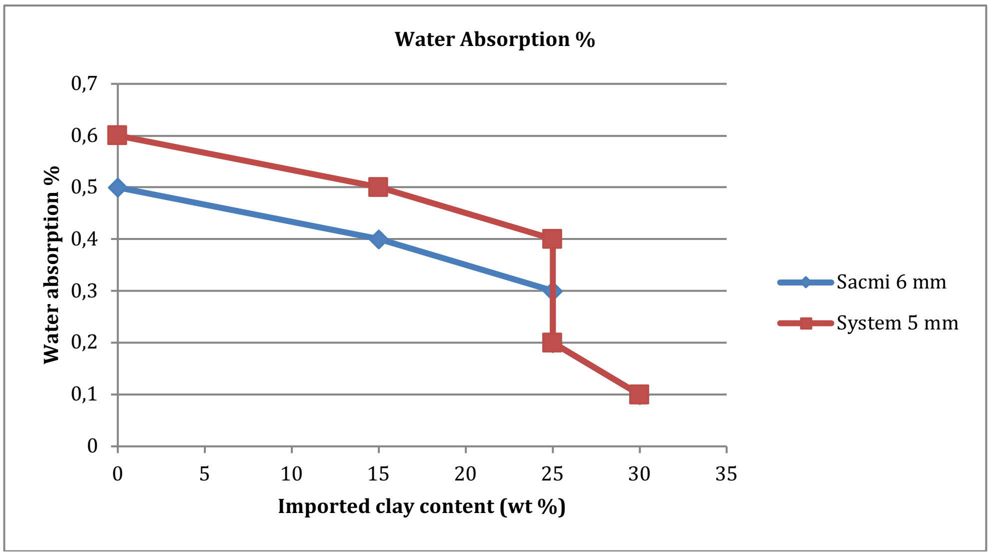

Figure 4. *Effect of imported clay content on water absorption for 5-6 mm thickness prototypes.*

4.2. MOR MODULUS OF RUPTURE

Test results for the Modulus of Rupture determination are presented in Figure 5 showing that there are no significant changes between manufacturers, but there is an improvement in product performance with the addition of imported clays, with a trend that is repeatable for the different thicknesses of the prototypes.

In the results obtained for breaking strength tests, a very marked tendency to improve mechanical properties can also be seen as the contents of imported clays increase, which is in line with the results of the water absorption. This effect is shown in Figure 6, which groups the results for the three thicknesses developed in the prototypes.

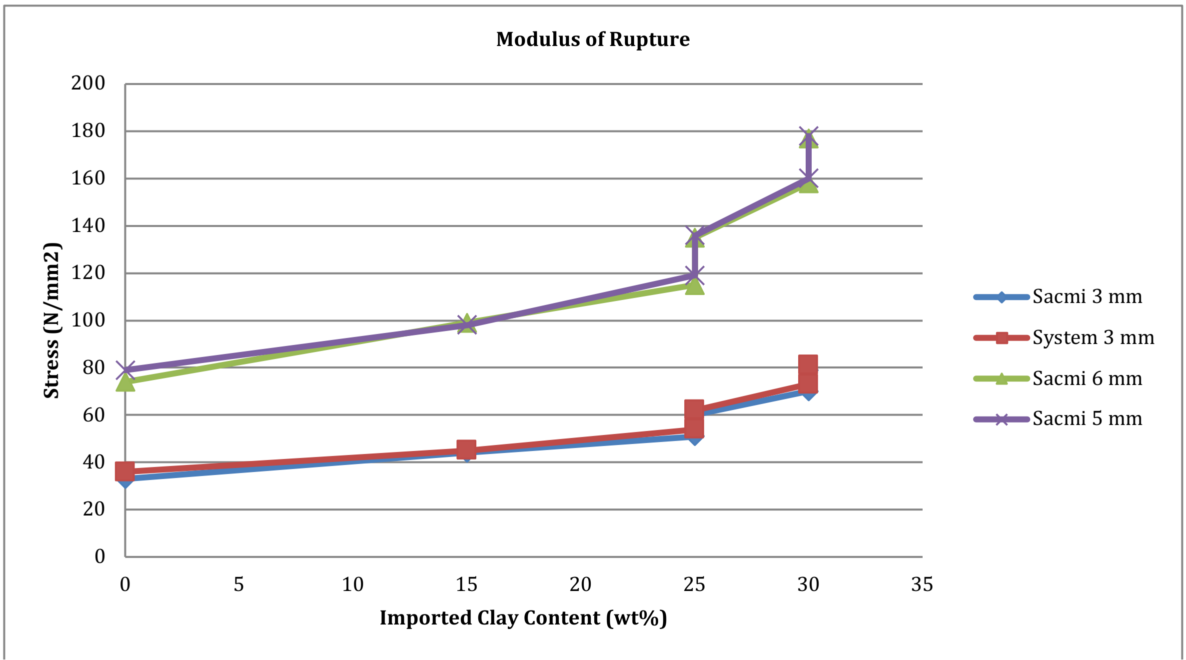

Figure 5. *MOR results for samples with thickness of 3, 5 and 6 mm.*

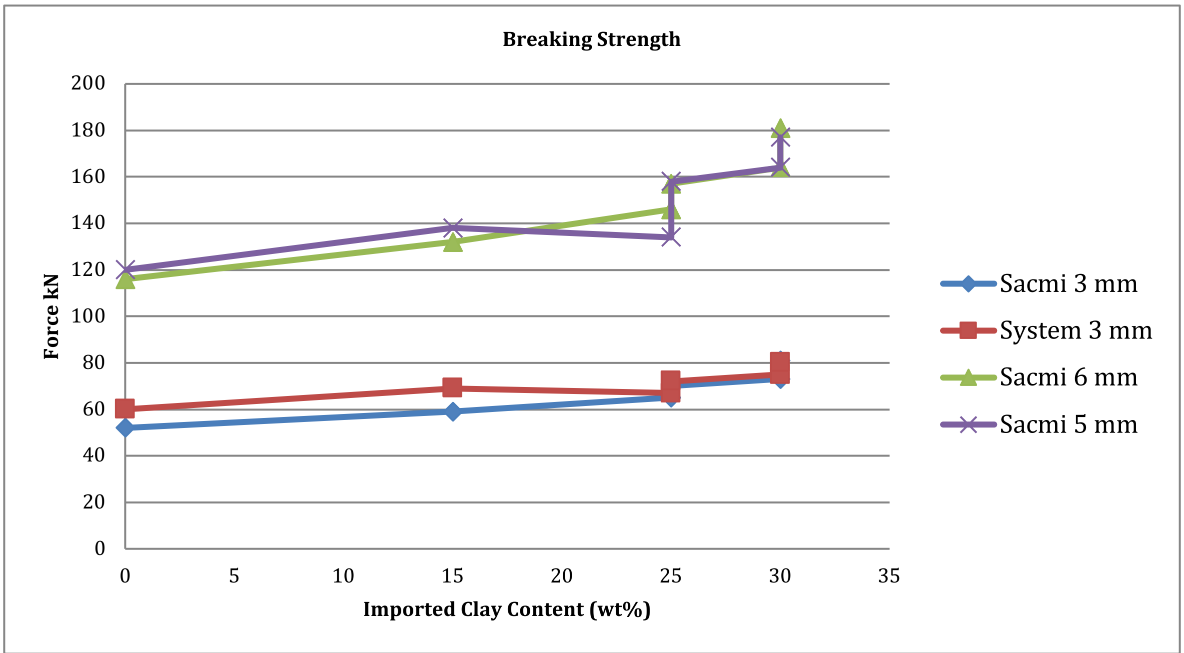

Figure 6. *Breaking strength results for samples with thickness of 3, 5 and 6 mm.*

5. CONCLUSIONS

Water absorption tests allowed all prototypes to be classified as porcelain tiles, with a water absorption % of less than 0.5%, except those manufactured with the composition of sample 1, which were classified as stoneware for all the thicknesses produced, and the composition of sample 2 for the thickness of 3 mm. This same composition, for thicknesses of 5 and 6 mm lay within the classification limit for porcelain tiles.

Mechanical performance tests did not yield significant differences when comparing between manufacturers; however, compositional variations greatly affect the values of the modulus of rupture and breaking strength.

Despite the above, in the case of the MOR, all prototypes reached the minimum that is specified for porcelain of normal thickness (10 mm), achieving values quite higher than the specification limit.

For the breaking strength, the values achieved by most 3 mm thickness prototypes do not reach the minimum value that has been proposed for this type of product, a case that is repeated for thicknesses of 5 and 6 mm.

The initial overall performance of the prototypes developed offers a very promising prospect for the Mexican ceramics sector, since, despite the replacement of Mexican by imported clay, the amount of Mexican raw materials that were integrated into these products ranged from 55 to 85% of the total mass of prototypes.

It is possible that, through a more detailed formulation, knowing the preliminary values reported here to be used as a benchmark, and by investing in technology transfer with the companies that manufactured these products, Mexico will continue to be one of the main producers of ceramic tiles, now by including tiles in the segment of large-format tiles and nominal "ultra-thin" thicknesses.

6. ACKNOWLEDGMENTS

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