THE MICROGRANULATION PROCESS: A TECHNOLOGY FOR DECARBONISING THE CERAMIC INDUSTRY. PRODUCT CHARACTERISATION

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ABSTRACT

The most commonly used process in manufacturing ceramic tiles involves preparing body compositions by wet grinding prior to spray drying the suspensions, known as the wet method, followed by firing of the glazed bodies in a single step (single firing). This manufacturing process calls for significant consumption of energy and natural resources, including water. Average water consumption per square metre tile is around 20 litres, while energy consumption is around 32 kWh per square metre tile.

The largest amount of energy consumed (almost 90%) is thermal energy through natural gas combustion, so improvement efforts in the quest to decarbonise the industry need to be aimed mainly at reducing heat energy consumption. The two stages that consume the most thermal energy are the spray drying of body suspensions (35%) and firing (55%). An alternative technology to the wet process as a way of preparing raw materials for the ceramic body is microgranulation, as it has the advantage of simultaneously reducing both CO_2 emissions and energy costs.

This paper presents a comparative analysis of granule properties, as well as of unfired and fired tiles made by the wet method and by microgranulation, with the singularity that the materials under study were produced on an industrial scale.

1. INTRODUCTION

In Europe, the most widely used process in manufacturing both glazed and unglazed ceramic tiles is the so-called wet method, by single firing [1]. This process produces granules with high flowability, which has enabled large-sized tiles to be manufactured thanks to the efficient way the granules are distributed in the press cavity. That, in turn, provides homogeneous distribution of unfired bulk density in the pressed tiles, which minimises, among other things, dimensional stability problems. The high flowability of this granulate has also allowed large ceramic slabs to be made, with forming technologies that do not confine the granulate inside a die.

The wet method entails a significant consumption of energy and natural resources, including water. Average consumption of water and energy per square metre tile is around 20 litres and 32 kWh, respectively [2].

About 60% of the water consumed is used in milling the body composition. Although a significant part of the water consumed is recycled [3], with certain types of bodies, the situation differs because the solids suspended in the water to be recycled may alter some properties in the end product, such as colour and fusibility, which therefore restricts wastewater recycling.

In regard to energy consumption, the largest proportion of energy consumed (90%) is thermal energy [2], so improvement efforts need to be mainly aimed at reducing the need for heat. The two stages that consume more than 90% of thermal energy are the spray drying of body suspensions (35%) and firing (55%). Although energy-saving measures continue to be implemented in single-deck furnaces [4], it is not currently foreseen that technologies for decarbonising tile firing are likely to emerge in the short or medium term that will result in significantly lower energy costs than at present.

Therefore, this study examines an alternative technology to the current system for preparing the tile body composition, with the aim of reducing the environmental loads associated with tile manufacturing, as well as the manufacturing costs. This involves significantly reducing water consumption to make the slurry drying phase unnecessary. The proposed process consists of grinding the raw materials in a pendulum mill, followed by microgranulation using a specifically developed process to obtain a press powder with similar flowability to that of spray-dried powder. The novelty of the work lies in the use of a micro granulate obtained at an industrial facility, operating non-stop, unlike other previously published papers that refer exclusively to studies undertaken on a laboratory or pilot scale [5, 6, 7].

2. EXPERIMENT

2.1 MATERIALS

The study was carried out using an industrial spray-dried powder (AT) obtained by the wet method, used to manufacture glazed red-firing stoneware tile, in which local red illitic-kaolinitic clays with variable quantities of quartz are used. A micro granulate (mGR), which is also employed in the manufacture of red stoneware tile and was obtained at the industrial facility described in Section 3, was also used. Figure 1 shows the physical appearance of both materials.

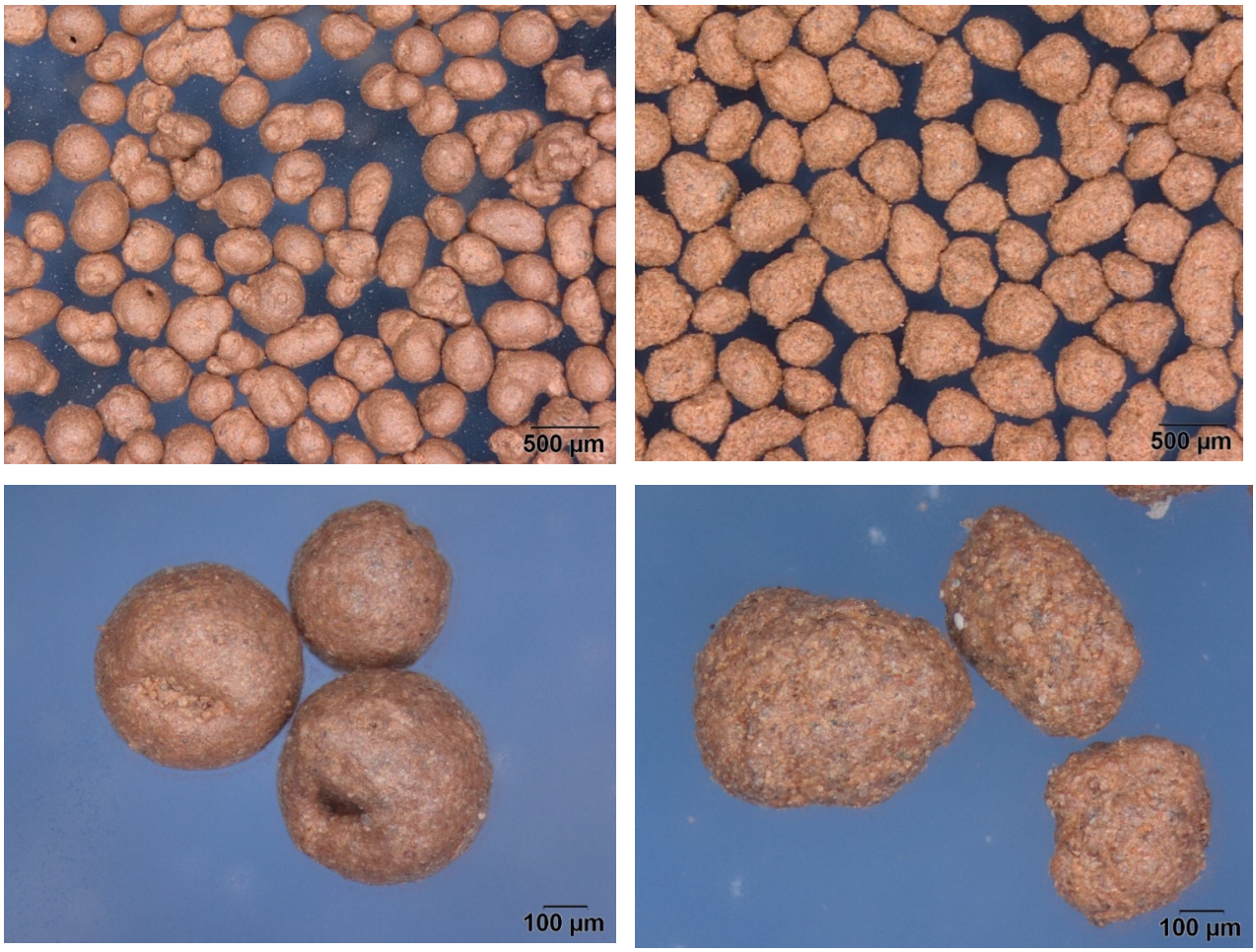


Figure 1. *Appearance of the 300-500 µm spray-dried powder fraction and of the micro granulate.*

2.2 EXPERIMENTAL PROCEDURE

The experimental work consisted of characterising both granulates by evaluating the following features:

- Granule characterisation
  - ✓ Flowability
  - ✓ Granule hardness
  - ✓ Granule size distribution
- Unfired behaviour
  - ✓ Compaction diagram
  - ✓ Dry mechanical strength
  - ✓ Permeability
  - ✓ Observation with microscope
- Firing behaviour and final properties
  - ✓ Vitrification diagram
  - ✓ Observation and photography with an electron microscope

The procedures used for these tests are briefly described below.

Determination of flow rate

To calculate the flow rate, a flowmeter (Figure 2) consisting of two glass funnels with a top diameter of 15 cm, a height of 15 cm and a discharge angle of 25° was used. The test process consists of pouring the material into the upper funnel and then activating the device that enables the material to flow into the lower funnel. When all the material has run through, the lower funnel hatch is opened, and the time taken to empty the funnel is read. To calculate volumetric flow rate, free-fall bulk density is measured in a 200 cm^3 test tube Figure 2). Mass flow rate (v_{FM}) and volumetric flow rate (v_{FV}) are defined as:

$$v_{FM} = \frac{m}{t_F} \qquad v_{FV} = \frac{V}{t_F} = \frac{m}{t_F \cdot \rho_0}$$

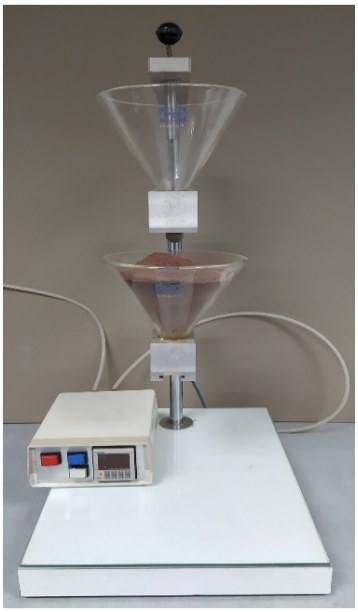
where:

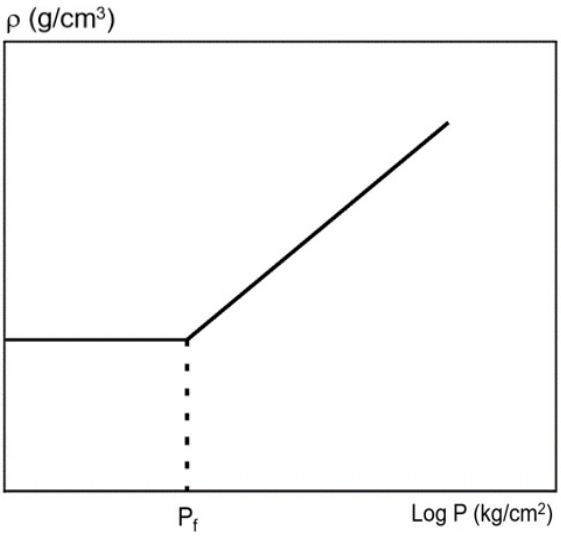
m: mass of discharged solids (g)

t_F: discharge time (s)

V: volume of discharged solids (cm^3)

ρ_0: bulk density of free-fall filling (g/cm^3)





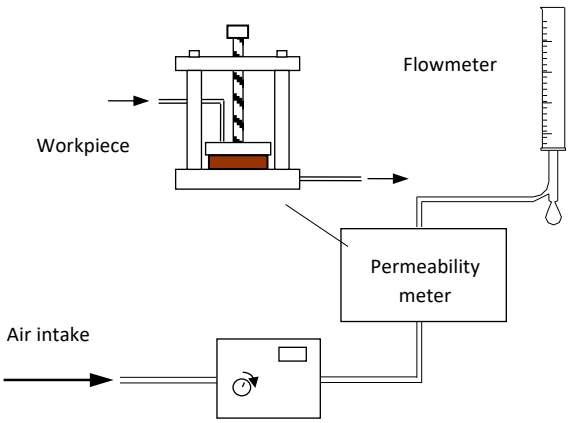


Figure 2. *Glass flowmeter used in the flow rate measurements, bed density measurement, compaction diagram and scheme of the permeability reading procedure.*

Determination of granule hardness

Granule hardness was determined on a universal test machine at a travel speed of 2 mm/min. The test consists of forming a test specimen by pressing, such that the pairs of values, applied load/granule bed height, are recorded. From these values, a graph similar to the one shown in Figure 2 is obtained, where bed density (ρ) is plotted as a function of the logarithm of pressure (P). The intersection of the two sections of the graph is defined as the yield point or pressure (P_f). This value relates directly to the hardness or mechanical strength of the granules.

Compaction diagram

To determine the compaction diagram, cylindrical specimens (4 cm in diameter and approximately 7 mm thick) were formed at a moisture content of 5.5% (dry basis) for the spray-dried powder and 6.5% for the micro granulate at different pressing pressures. The specimens were dried at 110°C in an electric laboratory kiln with air recirculation. Subsequently, they were weighed, and their dry bulk density was determined using the mercury immersion method.

Dry mechanical strength

Dry mechanical strength was determined by three-point bending. To do so, prismatic specimens, 80 mm long, 20 mm wide and approximately 7 mm thick, were formed by uniaxial pressing under the conditions described above at a pressure of 250 kg/cm^2. The test specimens were dried at 110°C in an electric laboratory kiln with air recirculation.

The tests were carried out on a universal mechanical test machine at a constant deformation rate of 1 cm/min.

Coefficient of permeability

To determine permeability, cylindrical test specimens (4 cm in diameter and approximately 7 mm thick) were formed by uniaxial pressing under the conditions described above at a pressure of 250 kg/cm^2.

To carry out the test, a dry workpiece, the side surface of which had been pre-sealed to prevent any air loss, was inserted in the permeability cell, as shown in Figure 2. By suitably adjusting the pressure regulation valve, a pressure gradient across the workpiece is set on the pressure gauge. Then, for each value in the pressure gradient, the time taken for a perfectly measured volume of air to flow through the workpiece is measured with the flowmeter. Measurements are taken with at least five different pressure gradients for each test specimen.

Permeability is calculated from the equation:

$$K_p = \frac{2 \cdot \mu_a \cdot Q_a \cdot L}{S} \cdot \frac{P_{atm}}{(P_1^2 - P_2^2)}$$

where:

K_p: Permeability (m^2)
μ_a: Air viscosity at working temperature (N·s/m^2)
Q_a: Air flow rate (m^3/s)
L: Specimen thickness (m)
S: Section of air passage (m^2)
P_1: $P_{atm} + \Delta P$ (N/m^2)
P_2= P_{atm}: Atmospheric pressure (N/m^2)
ΔP: Set pressure difference (N/m^2)

Vitrification diagram

To determine firing behaviour, cylindrical test specimens (4 cm in diameter and about 7 mm thick) were formed by uniaxial pressing under the conditions described above at a pressure of 250 kg/cm^2. Firing was carried out at different temperatures in an electric laboratory kiln with a fast-firing cycle and dwell at maximum temperature of 6 minutes. The heating rate was 25ºC/min.

Fired mechanical strength

Fired mechanical strength was determined by three-point bending of specimens fired at 1130ºC.

3. DESCRIPTION OF THE MICROGRANULATION PROCESS

The microgranulation technology developed and patented by Granulation System consists of 3 main stages (Figure 3). First, the ceramic composition is ground in a Granulation System vertical pendular mill (GS-VM200). Micronisation can produce ground material with a size of less than 45 microns and final moisture content of less than 1%. The ground material is then fed into the microgranulator (GS-G200), where the micro granulate is generated using only water. The resulting product is a micro granulate with a moisture content of 12% and size between 125 microns and 1 millimetre.

Excess moisture in the micro granulate is removed in the fluidised bed dryer. The dryer (GS-S200) has been developed exclusively for Granulation System's microgranulation process and allows waste heat from other thermal processes or electric drying to be used, leaving the micro granulate at the optimum moisture content for pressing.

The entire microgranulation process is patented worldwide by Granulation System and complies with European standards for total decarbonisation in the raw materials preparation process for the ceramic industry.

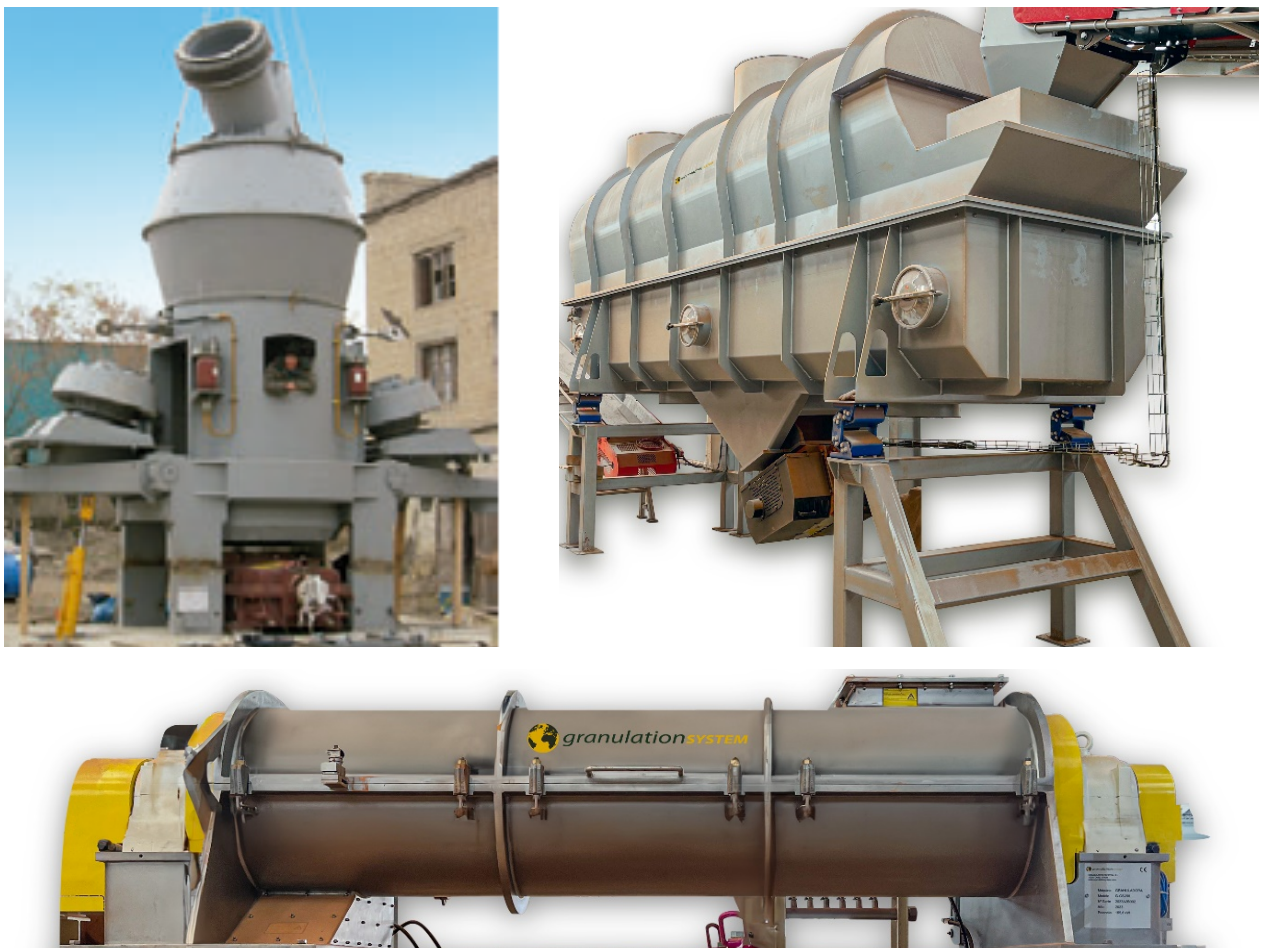


Figure 3. *GS-VM200 vertical mill (top left), GS-S200 dryer (top right) and GS-G200 microgranulator (bottom)*

4. RESULTS AND DISCUSSION

4.1 GRANULATE CHARACTERISATION

The granule size distribution of both materials is shown in Figure 4, in which great similarity can be seen between the granule size curves. Table 1 shows the flow rate and bed density values for both materials. It should be noted that, during discharge, both samples displayed a mass discharge pattern in which all the granules of material moved uniformly from the inlet to the outlet. The micro granulate can be seen to have slightly higher filling density (ρ_0), owing to the absence of the characteristic hollow centre of spray-dried material, while flowability is seen to be practically the same in both materials.

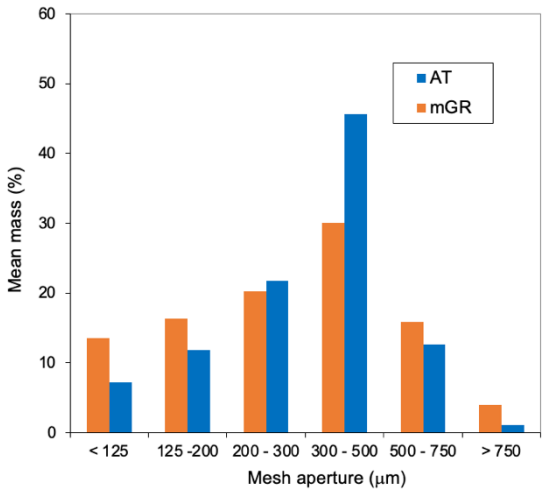


Figure 4. *Granule size distribution*

Sample	Moisture content (%)	ρ_0 (g/cm^3)	V_{FM} (g/s)	V_{FV} (cm^3/s)
AT	5.5	1.090 ± 0.010	33.0 ± 1.1	30.3 ± 1.2
mGR	6.5	1.127 ± 0.011	33.0 ± 1.1	29.3 ± 1.3

Table 1. *Bed density and flowability values*

With regard to other granulate properties (Table 2), it can be seen that the micro granulate has a higher content of particles larger than 63 µm as well as lower after-pressing expansion and granule hardness values, which should ensure microgranule deformation when tiles are pressed.

Composition	AT	mGR
Moisture content (%)	5.5	6.5
Residue on 63 µm (%)	8.6	13.5
Carbonates (%)	2.5	1.7
Vibrated bed density (g/cm³)	1.148 ± 0.011	1.193 ± 0.007
Diametral expansion (%)	0.49 ± 0.08	0.30 ± 0.08
Axial expansion (%)	8.9 ± 0.9	8.8 ± 0.8
Yield pressure (kg/cm²)	4.1 ± 0.2	3.6 ± 0.2

Table 2. *Unfired composition properties*

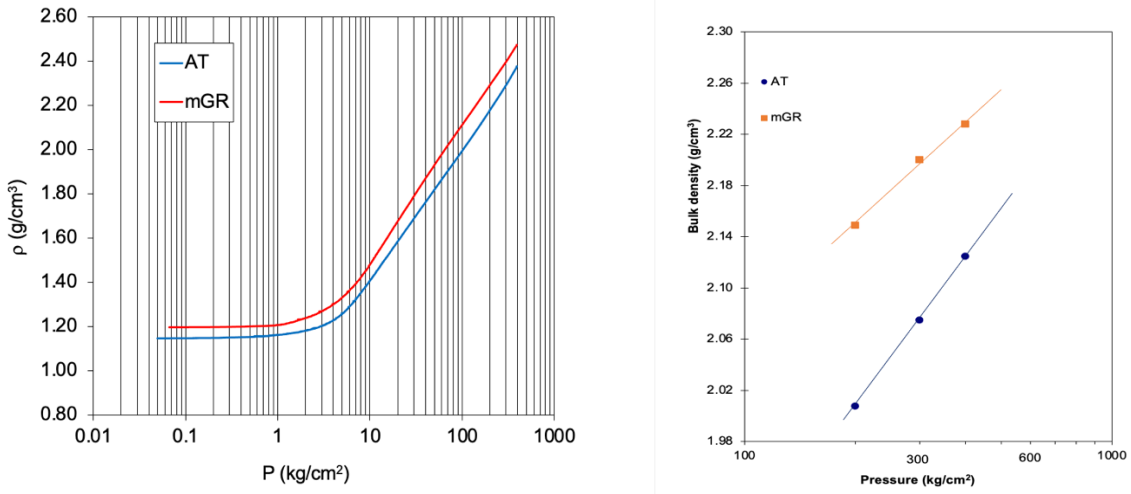


Figure 5. *Evolution of bulk density of the bed (left) and of the workpiece (right) with pressing pressure.*

4.2 UNFIRED BEHAVIOUR

The unfired behaviour values for the spray-dried powder and micro granulate are shown in Figure 5 right (compaction diagrams) and Table 3 (dry properties of the formed test specimens).

The micro granulate is seen to provide the workpieces with higher dry bulk density, which is due to its higher moisture content and especially to its higher density as a result of the absence of the characteristic hollow centre of spray-dried powder [8]. The higher dry bulk density of the specimens made with microgranules gives them greater mechanical strength, but also lower air permeability, an issue that needs to be regulated by adjusting the pressing pressure to balance both properties.

Scanning electron microscopy was also used to observe the fresh fracture of the dried workpieces (Figure 6), and in both cases the presence of a clay matrix can be observed, in which the remains of granules that have not been completely deformed are noted. This is due to the fact that the size distribution and hardness of both granulates is very similar, unlike that observed with other types of granulation systems that produce microgranules with greater hardness [7].

Composition	AT	mGR
Moisture content (%)	5.5	6.5
Pressure (kg/cm^2)	250	250
Dry bulk density (g/cm^3)	2.042	2.174
Dry mechanical strength (kg/cm^2)	29	34
Coefficient of air permeability (Kp) (m^{2}x10^{16})	1.80	1.21

Table 3. *Unfired behaviour of the compositions*

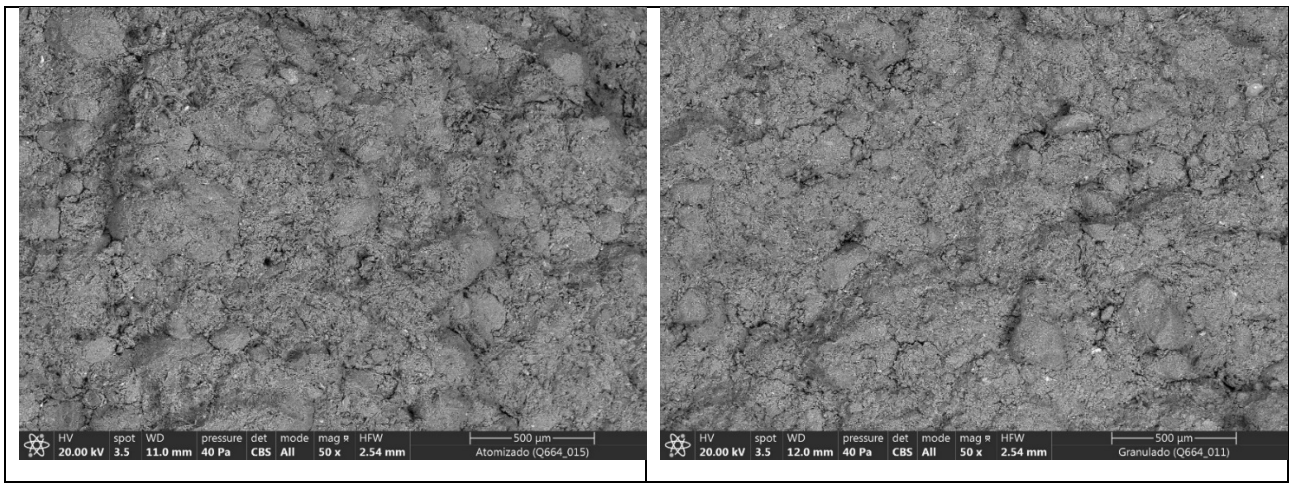


Figure 6. *SEM micrographs of the cross-section of unfired AT (left) and mGR (right) samples*

4.3 FIRING BEHAVIOUR AND FINAL PROPERTIES

Figure 7 shows the vitrification graphs. It can be seen that the evolution with temperature of linear shrinkage and water absorption in the pieces made with spray-dried powder is faster than in those made with the micro granulate, as the raw materials composition was not the same in the two cases and because of the absence of deflocculant in the micro granulate which, on being a sodium salt, acts as a flux. On the other hand, the micro granulate displays lower linear shrinkage across the entire temperature range, because the specimens are more compact.

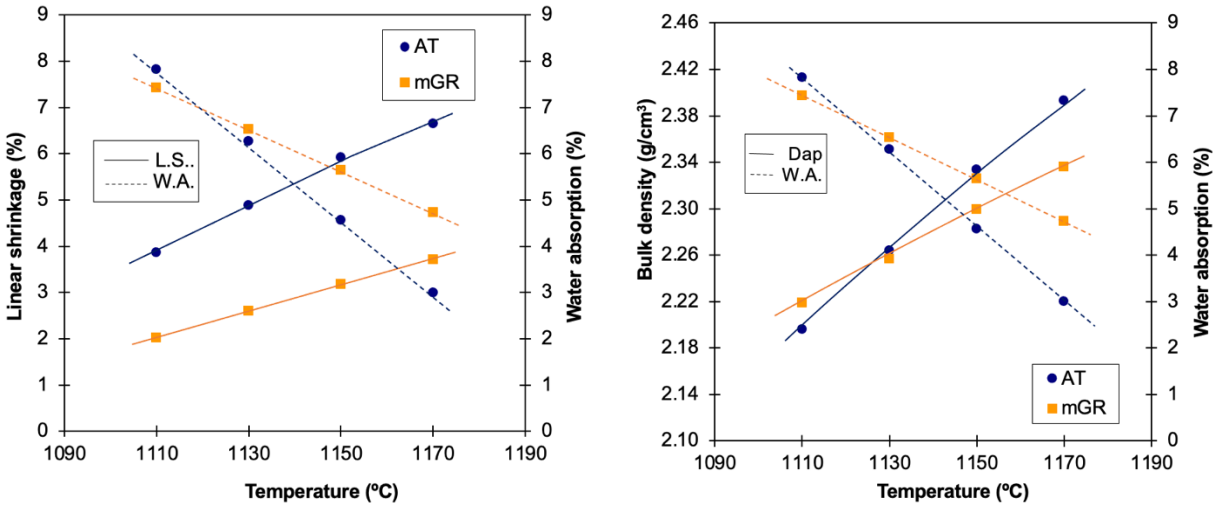


Figure 7. *Evolution of linear shrinkage, bulk density and water absorption with temperature*

In order to compare the final properties of the fired pieces made with the two materials, the temperature at which 6% water absorption is obtained was selected as the reference temperature, since this is the limit value for classifying ceramic tiles in group BIIa. The properties of the pieces were calculated at that temperature, as detailed in Table 4.

It can be seen that the micro granulate provides the required water absorption at practically the same temperature, but with less firing shrinkage, as mentioned above. Bulk density is practically the same in both fired pieces.

Composition	AT	mGR
Temperature (ºC)	1132	1139
Linear shrinkage(%)	5.0	2.9
Loss on ignition (%)	4.8	4.5
Bulk density (g/cm³)	2.270	2.275

Table 4. *Properties at 6% water absorption*

5. CONCLUSIONS

This study involves a comparative analysis of the technical properties of two granulates, one obtained by spray drying and the other by microgranulation. The following conclusions may be drawn:

- ✓ Spray-dried powder exhibits a characteristic hollow centre, whereas the micro granulate is solid and therefore denser. Both granulates exhibit similar flowability, which ensures appropriate distribution in the press cavity.
- ✓ Micro granulate hardness is slightly lower than that of the spray-dried powder, which facilitates deformation and granule breakage during pressing.
- ✓ The properties of the unfired pieces vary as a function of the granules used. Thus, the piece made with micro granulate provides higher bulk density and dry mechanical strength, and also lower permeability when working at constant pressure. These characteristics can be adjusted by regulating pressing conditions.
- ✓ A water absorption value of 6% is achieved at a similar temperature with both granulates. At that temperature, bulk density is almost identical, but the shrinkage displayed by microgranulation is clearly lower, as a result of the higher dry bulk density of the pieces.

6. REFERENCES

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