

USE OF SODIUM CARBONATE AS A BINDER IN CERAMIC TILE COMPOSITIONS

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ABSTRACT

This study analyses, first, the influence of sodium carbonate content on the behaviour of the ceramic tile body composition during the different manufacturing process stages (preparation of the suspension, pressing, and firing), as well as on unfired tile mechanical strength. It has been verified that sodium carbonate can be used as a binder in ceramic tile compositions, since small percentages considerably enhance dry tile mechanical strength. It has furthermore been determined that for each composition there is an optimum addition content, with high increased mechanical strength (up to 70%), without this noticeably affecting the rheological behaviour of the suspension to be spray dried. These results are currently being patented (patent application^o P200930148).

Once the binding effect of sodium carbonate had been verified, it was sought to establish its action mechanism. For this purpose, drops of mixtures of a standard ceramic composition and increasing quantities of sodium carbonate were prepared. The drops were rapidly dried and the granules were characterised by scanning electron microscopy. It was thus verified that the most likely sodium carbonate action mechanism was formation of solid bridges by crystallisation.

1. INTRODUCTION

In recent years, ceramic tile size has evolved greatly, sizes even larger than 60x120 cm being made, with increasingly smaller thicknesses. At the same time, the introduction of new decorating techniques, such as dry colouring of spray-dried powder granules, has led to an important loss (up to 30%) of the mechanical strength of dry tile bodies fabricated using this technology [1][2]. As a result, ceramic tile manufacturing companies have begun to detect an increase in the percentage of breakages in the pre-firing stages, leading to decreased productivity and higher manufacturing costs. As a result, there is growing interest in the search for materials that enhance the mechanical strength of unfired ceramic tiles.

Clay materials are the system binder, par excellence, of ceramic tile body compositions [3]. Therefore, faced with the need to increase their mechanical strength, the most immediate option would be to raise the quantity of these raw materials in the formula. This change in formula, however, would entail changes in composition behaviour in the different process stages, as well as in tile properties. That is why organic admixtures (such as acrylic polymers) and inorganic admixtures (such as compounds derived from boron) are being increasingly used. With regard to acrylic polymers, these act as suspension dispersants [4] and raise tile mechanical strength before firing. However, one of the disadvantages of organic binders is that they can increase the tendency for 'black core' to form in the tiles. On the other hand, with regard to inorganic binders, their main disadvantage is that they sometimes alter the rheological behaviour of the suspension.

In view of the above, inorganic binders are of greater interest for the manufacture of ceramic tiles, provided that they do not adversely affect the rheological behaviour of the suspension. One of the main bonding mechanisms of these binders is by the formation of solid bridges between particles [5]. Solid bridges can form by chemical reactions, by crystallisation, or by solidification and are one of the most powerful existing bonding mechanisms [6].

The most widely used process for fabricating ceramic tile bodies in Spain consists of wet milling, followed by spray drying of the resulting suspension. The spray-dried powder obtained (with a moisture content ranging from 5,5 to 6,5%, on a dry basis) is used to form tile bodies by uniaxial pressing in hydraulic presses. Given the characteristics of this process, it is clear that inorganic binders that form

solid bridges by crystallisation could be highly effective. Indeed, crystallisation processes consist of the formation of crystals from a solution [7]: as a result, if during milling, or by dispersion in the resulting suspension, a compound is added that displays a high tendency to crystallise, this phenomenon may be expected to take place during the spray-drying process.

The use of sodium carbonate as a dispersant in ceramics compositions is well known, and is also one of the classic examples in the literature consulted on crystallisation [8]. Figure 1 shows the phase diagram of the system $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ [8], which clearly displays a high tendency to crystallise. The crystalline phase that forms differs, depending on the temperature, ranging from the decahydrate compound ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) to the anhydrous one.

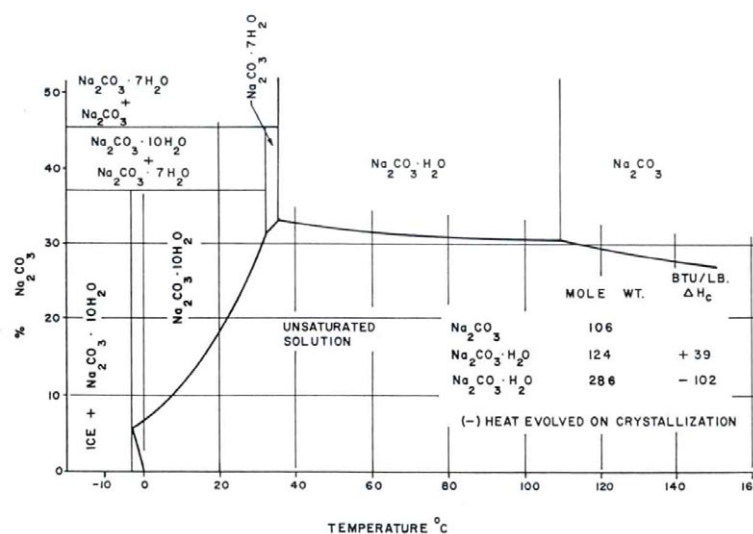


Figure 1. Phase diagram of the system $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ [8].

In previous (unpublished) tests, it was verified that sodium carbonate, under certain conditions, exhibited a bonding effect in ceramic body compositions, though the action mechanism had not been established to date; nor have been studies been found in the literature surveyed that address their use as binders in this type of composition. This study was therefore undertaken with a view to verifying the bonding effect of sodium carbonate in white-firing earthenware wall tile and glazed porcelain tile compositions. These two products were chosen because they have the highest dry mechanical strength requirements: the former because larger and larger sizes are being fabricated and the latter, in addition to the same reason, because of the widespread use of the dry-colouring technique (a technique that, as noted above [1][2], reduces tile body mechanical strength).

2. EXPERIMENTAL

The study was conducted with a commercial sodium carbonate sample (99% purity), a mixture of the raw materials used in industrial practice to produce white-

firing earthenware wall tile bodies and an industrial suspension used to produce spray-dried powder for glazed porcelain tile manufacture.

In the first part of the study, different quantities of sodium carbonate were added to the earthenware tile raw materials mixture with a view to determining the optimum addition (i.e. the sodium carbonate percentage that improved dry tile mechanical properties without excessively impairing suspension rheological behaviour). The characterisation of the compositions consisted of determining their deflocculation curves and then, under appropriate viscosity conditions, of preparing suspensions from the compositions by wet milling. The suspensions were spray dried and the resulting spray-dried powders were characterised by determining their pressing behaviour and the dry mechanical strength of test pieces formed at the same bulk density (by three-point bending). The experimental procedures used to determine these properties have been described elsewhere [9][10]. The optimum percentage obtained was then added to the industrial suspension for glazed porcelain tile manufacture. Both the initial suspension and the suspension obtained after the sodium carbonate addition were characterised by the relevant tests for earthenware wall tile compositions.

In the second part of the study, an industrial trial was conducted with the earthenware wall tile composition. The trial consisted of milling the wall tile composition in a batch mill, on the one hand adding 0,3% sodium carbonate and, on the other, adding a binder of an organic nature. The resulting suspensions were spray dried and the resulting spray-dried powders were used to produce earthenware wall tiles, determining their pressing behaviour, dry mechanical strength, and tendency to form black core on a laboratory scale. This last test was carried out by forming test pieces at a much higher dry bulk density than that used industrially and firing these test pieces in an accelerated cycle that prevented total oxidation of the organic matter [10].

Finally, in the third part of the study, various experiments were performed to establish the sodium carbonate action mechanism. These experiments consisted of determining the crystalline phases obtained by the crystallisation of saturated solutions of sodium carbonate in water at different temperatures, and of observing different materials (from sodium carbonate crystalline aggregates to the granules obtained with the porcelain tile composition and different sodium carbonate additions) in a scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Determination of the optimum addition to the earthenware wall tile composition.

3.1.1. Rheological behaviour.

The deflocculation curves (variation of viscosity with the added deflocculant

percentage) of the earthenware wall tile composition with different sodium carbonate additions have been plotted in figure 2. The objective of the test was to determine the solids content that would allow a viscosity between 300 and 700 cP to be reached at the curve minimum (typical range of viscosities of industrial suspensions of white-firing compositions).

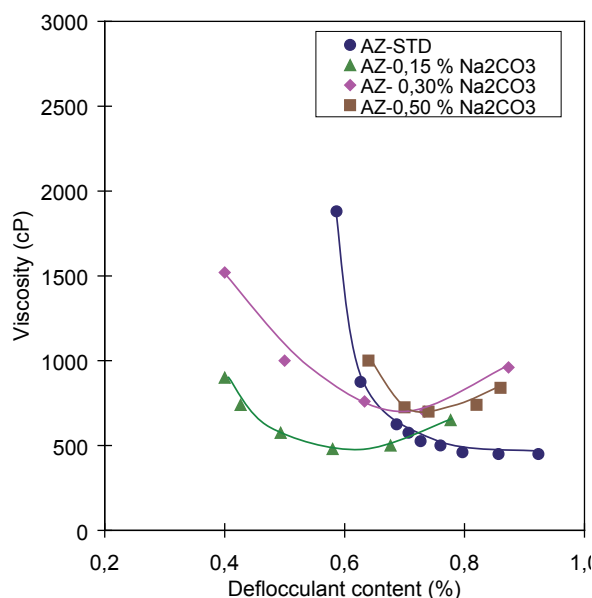


Figure 2. Deflocculation curves of the earthenware wall tile composition with different sodium carbonate contents.

Table 1 details the solids content reached with each composition and the deflocculant content at which the minimum viscosity was found. The results indicate that sodium carbonate additions up to 0.3% do not significantly modify minimum viscosity, deflocculant consumption decreasing slightly in relation to the composition without carbonate. No suspension ageing is observed in this range of additions according to the thixotropy data. At sodium carbonate additions exceeding 0.3%, the rheological behaviour worsened, with a decreasing solids content at which the required viscosity values were obtained. This behaviour occurs because sodium carbonate is a deflocculant, and, as indicated above, has been traditionally used as such in ceramic compositions. Thus, this electrolyte modifies the clay particle surface charge and introduces Na⁺ cations. It also precipitates the Ca²⁺ ions in the suspension in the form of CaCO₃, which facilitates their replacement with Na⁺ ions at the particle surface. Rheological behaviour worsens with additions exceeding 0.15% and, in a more pronounced form with additions exceeding 0.3% (over-deflocculation), because the action mechanism is exclusively electrostatic and non-steric, there being a reduction in the absolute value of the zeta potential once the optimum addition has been exceeded [9][11].

Composition	AZ-STD	AZ-0.15Na ₂ CO ₃	AZ-0.30Na ₂ CO ₃	AZ-0.50Na ₂ CO ₃
Solids content (%)	70.2	70.1	70.1	68.1
Deflocculant content (%)	0.80	0.63	0.73	0.74

Table 1. Deflocculation behaviour of the earthenware wall tile composition with different sodium carbonate additions.

3.1.2. Pressing behaviour and unfired tile properties.

With the spray-dried powders obtained from the suspensions characterised in the previous section, test pieces were formed by pressing under the conditions described in table 2 and their dry mechanical strength was determined. The results show that the sodium carbonate addition to the earthenware wall tile composition in the tested percentage practically does not affect the pressing behaviour of the spray-dried powders, a slight reduction even being observed in the required pressing pressure in order to reach a dry bulk density of 1,95 g/cm³ in relation to the composition without sodium carbonate. This bulk density was chosen for the determination of dry mechanical strength, since it may be considered representative of the industrial forming conditions of white-firing earthenware wall tile bodies.

The mechanical strength data indicate that as the sodium carbonate content increases, the mechanical strength of the tiles also increases, a 0.3% sodium carbonate addition providing a 31% increase in mechanical strength compared with that of the spray-dried powder without sodium carbonate. For the spray-dried powder with 0.5% sodium carbonate, the increase in mechanical strength is even greater (50%), but it must be borne in mind that with this percentage, the rheological behaviour worsens.

Composition	AZ-STD	AZ-0.15Na ₂ CO ₃	AZ-0.30Na ₂ CO ₃	AZ-0.50Na ₂ CO ₃
Moisture content (%)	5.5	5.5	5.5	5.5
Pressure (kg/cm ²)	240	210	220	220
Dry bulk density (g/cm ³)	1.951	1.946	1.950	1.951
Dry mechanical strength (kg/cm ²)	36	32	47	54

Table 2. Properties of unfired spray-dried earthenware tile powders with different sodium carbonate additions.

From this part of the study, it may be concluded that the optimum sodium carbonate addition for the earthenware wall tile composition used was 0.30%, since it significantly enhanced tile dry mechanical strength without impairing the rheological behaviour of the body suspension.

3.2. Sodium carbonate addition to the porcelain tile composition.

3.2.1. Rheological behaviour.

When the optimum percentage of sodium carbonate (0.3% with respect to the solid) is added to the industrial porcelain tile suspension, viscosity increases slightly (figure 3). Although the resulting value was in the typical range of such industrial suspensions, the variation in viscosity with the added deflocculant percentage (the same used industrially in milling the starting composition) was studied. The results show that at a 0.2% deflocculant addition, viscosity minimises (for the suspension starting solids content), this value lying within the representative range used in industrial practice.

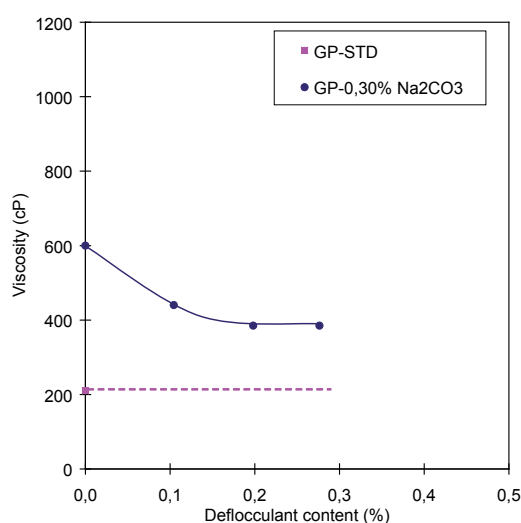


Figure 3. Rheological behaviour of the porcelain tile composition with and without the sodium carbonate addition.

Since the suspensions sometimes remain in stirring tanks for long times prior to spray drying, the evolution of viscosity and thixotropy of the two suspensions was determined with time [10]. For this purpose, the suspensions were kept for four days in a tank with a stirring system similar to that used in tanks on an industrial scale. Table 3 details the results. It may be observed that there were no important differences in the evolution of viscosity of the two suspensions with time. The fact that the resulting viscosity values are higher than those in figure 3 is due to the shear thinning behaviour of the clay suspensions. Thus, as a result of the higher shear rates in the case of the laboratory stirrer, the viscosity obtained was considerably lower than in the case of the tank.

Conditions	Initial conditions		2 days		4 days	
	Viscosity (cP)	Thixotropy (cP)	Viscosity (cP)	Thixotropy (cP)	Viscosity (cP)	Thixotropy (cP)
GP-STD	1400	1720	1600	1920	1720	2050
GP-0.30% Na ₂ CO ₃	1640	1840	1720	2000	1800	2150

Table 3. Evolution of the viscosity and thixotropy of the two porcelain tile suspensions with time.

3.2.2. Pressing behaviour and unfired properties.

The results of the determination of mechanical strength, shown in table 4, indicate that the addition of 0.3% sodium carbonate increases tile mechanical strength by practically 70% compared with that of the spray-dried powder without sodium carbonate. This increase is substantially higher than that obtained with the earthenware wall tile composition. It may be concluded, therefore, that the improvement of tile body mechanical strength with the sodium carbonate addition depends on the starting composition, though this improvement is always considerable (at a percentage of 0.3%).

Composition	GP-STD	GP-0.30% Na ₂ CO ₃
Moisture content (%)	5.5	5.5
Pressure (kg/cm ²)	330	340
Dry bulk density (g/cm ³)	1.953	1.950
Dry mechanical strength (kg/cm ²)	43	73

Table 4. Properties of unfired spray-dried porcelain tile powders with and without the sodium carbonate addition.

3.3. Industrial trial of the earthenware wall tile composition.

In the industrial trial, the processing behaviour of the earthenware wall tile composition used on a pilot scale was compared, when either the customarily used organic binder or sodium carbonate in the optimum quantity was added. The trial consisted of milling the earthenware wall tile composition in a batch mill with the two binders, and spray drying the resulting suspensions. The spray-dried powders obtained were used to fabricate earthenware wall tiles, and no differences were observed in their dimensional characteristics or in their properties. Nor were defects observed in the glazed surface of the tiles.

At the same time, a laboratory-scale characterisation was performed of both spray-dried powders by the determination of their tendency to form black core, of their pressing behaviour, and of their dry mechanical strength. The results indicate that, while the pressing behaviour of both spray-dried powders was very similar, the tiles obtained with the sodium carbonate-containing composition displayed slightly higher mechanical strength than that obtained with the composition containing the

organic binder (47 kg/cm² in relation to 45). With regard to the black coring tendency, a cross-section of the test pieces is shown in figure 4. As was to be expected, it may be observed that, owing to the inorganic nature of sodium carbonate, the extension of the oxidised area is larger, the sodium carbonate addition therefore exhibiting a smaller tendency to black core formation.

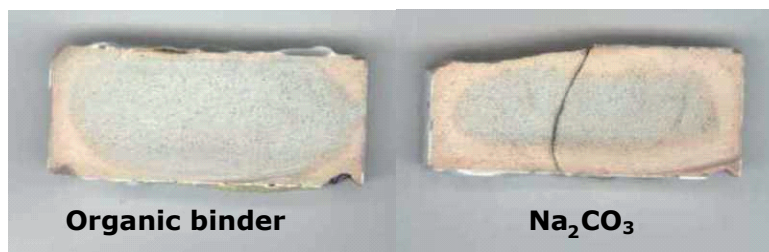


Figure 4. Cross-section of test pieces of white-firing earthenware wall tile obtained in the test of the tendency to form black core.

3.4. Action mechanism of sodium carbonate as a binder in ceramic tile body compositions.

The variation of the dry mechanical strength of test pieces of the earthenware wall tile composition with the added sodium carbonate percentage has been plotted in figure 5. The figure shows that at small sodium carbonate additions there is no improvement in mechanical strength, the binding effect being observed at additions above 0.2%. This coincides roughly with the proportioning percentage above which over-deflocculation begins to occur (table 1). As already noted, the sodium carbonate deflocculation mechanism consists of the modification of the clay particle surface charge and the precipitation of Ca²⁺ ions in the suspension in the form of CaCO₃, which facilitates their replacement with Na⁺ ions at the particle surface.

If, as postulated in the introduction, the sodium carbonate action mechanism occurs by the formation of solid bridges when sodium carbonate crystallises between the particles, it is reasonable to observe no binding effect at the percentages at which sodium carbonate acts as a deflocculant. This is because there must be free Na⁺ and CO₃²⁻ ions for sodium carbonate to crystallise, and this occurs when there is excess sodium carbonate.

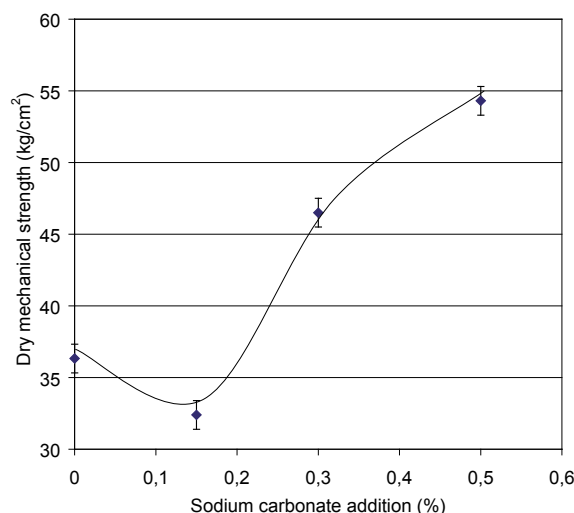


Figure 5. Variation of dry mechanical strength of the earthenware wall tile composition with the sodium carbonate addition.

This mechanism is consistent with the increase in mechanical strength observed when 0.3% sodium carbonate is added to the porcelain tile suspension, since, at that content (figure 3), over-deflocculation can already be observed (it is necessary to add 0.2% deflocculant to reach minimum viscosity).

In order to be able to confirm this action mechanism, crystallisation tests of sodium carbonate solutions were conducted at 30% by weight at room temperature and at 110°C, the crystalline phases formed in each case being determined by X-ray diffraction. The diffractograms obtained indicate that in the test at room temperature, the phases that formed were monohydrate compounds ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and a small quantity of heptahydrate ($\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$). In contrast, the phases that formed during treatment at 110°C were anhydrous sodium carbonate and sodium carbonate monohydrate. This is consistent with the consulted literature [12], since the phases detected in the test at room temperature are stable at temperatures below 109°C, and the anhydrous phase is the major phase at higher temperatures. Since the granule temperature, during the spray-drying process, does not exceed 90°C under normal conditions, the phase that mainly forms may be expected to be the monohydrate compound (thermonatrite), whose structure is displayed in Figure 6 together with the SEM image obtained of the crystals formed at room temperature (which mainly displayed this phase).

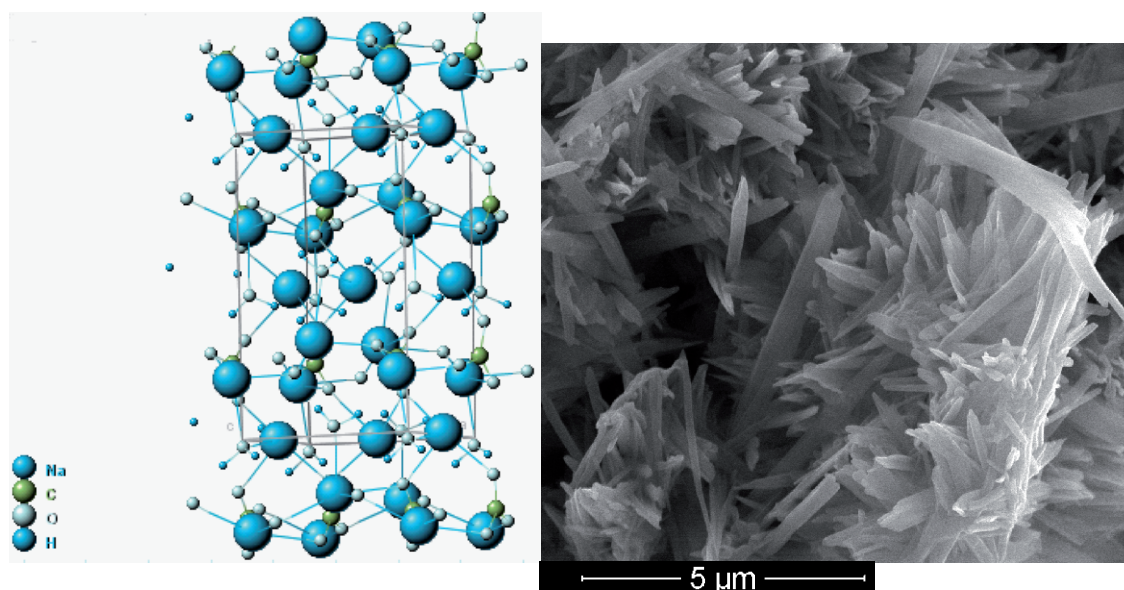


Figure 6. Thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) structure and SEM image of the crystals obtained.

If these acicular crystalline aggregates had formed in the granules of the different spray-dried powders that contained sodium carbonate, that would have been one of the main reasons for the higher mechanical strength. The surface and inside of granules of spray-dried porcelain tile powder with 0.3% sodium carbonate were observed by SEM. Figure 7 shows that there is no evidence of crystalline aggregate formation either at the surface or inside the granules. This could be due to the small quantity of sodium carbonate added. In order to verify this, granules were prepared from the industrial porcelain tile suspension, adding larger quantities than those used in the study (1, 3, and 5% by weight with respect to the solid).

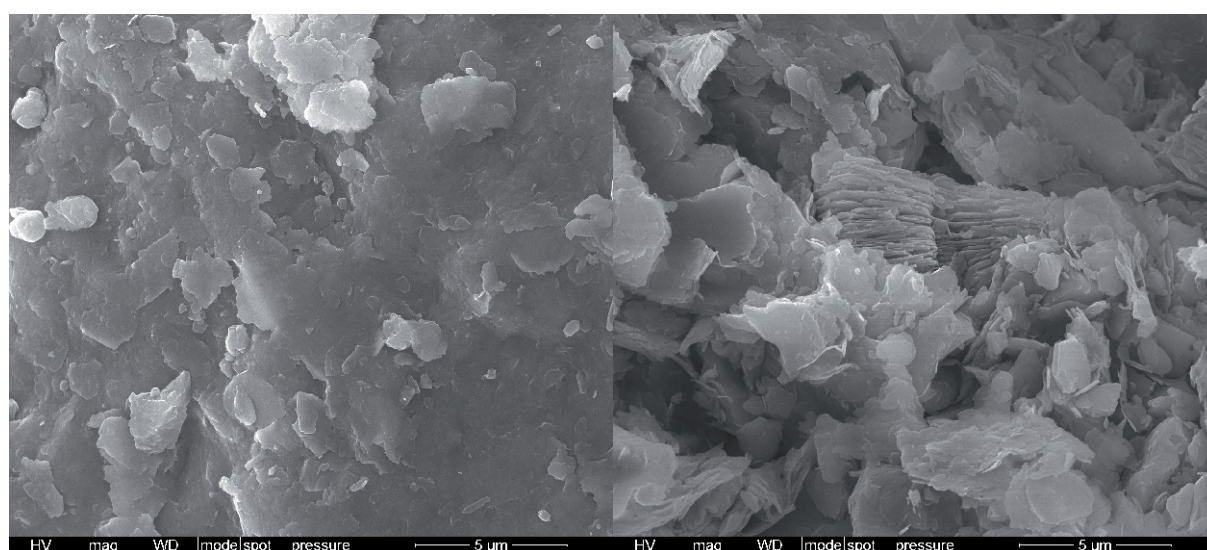


Figure 7. SEM images of the surface (left) and inside (right) of a granule of spray-dried earthenware wall tile powder with 0.3% sodium carbonate.

A graduated pipette was used to prepare the granules (figure 8), enabling drops of constant volume to be obtained, which were deposited on a waterproof surface. In order to be able to simulate the spray-drying process, in which the sprayed drops enter into contact with gases at temperatures between 300 and 500°C, the surface with the drops was set in an electric laboratory kiln with a chamber at 400°C. The drops dried in less than 1 minute.

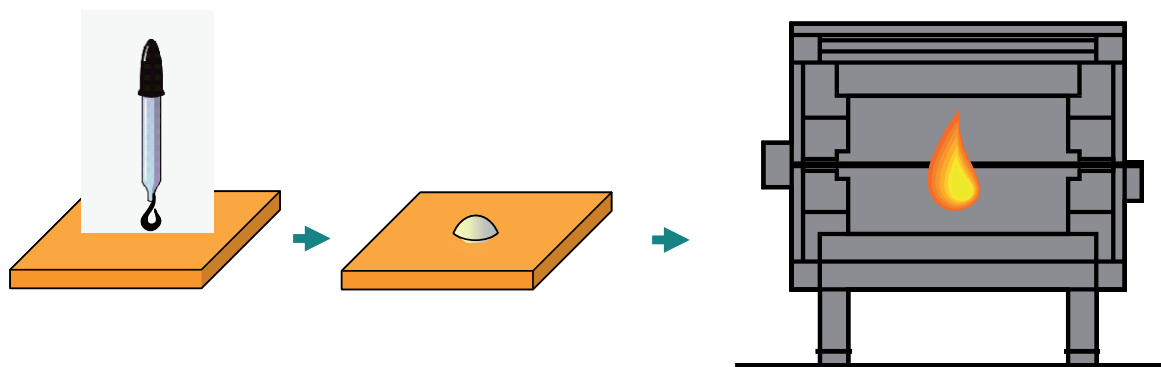


Figure 8. Schematic illustration of the process used to obtain granules with high Na_2CO_3 contents on a laboratory scale.

Figure 9 shows that the granules contain no acicular crystalline aggregates with any of the sodium carbonate additions, like those in figure 6. What may in fact be clearly observed in figure 9 (right image) is sodium carbonate crystallisation at the surface of the granule with 5% sodium carbonate (sodium carbonate crystallisation forming in some areas of the shell marked by arrows). Taking into account the characteristics of the process used to obtain these granules, while not yet having been able to verify the phases, the crystalline phases that must have formed are the anhydrous phase and the monohydrate compound (thermonatrite), just as in the sodium carbonate crystallisation test at 110°C. This crystallisation must have developed with all the sodium carbonate additions, including with the 0,3% addition (granules obtained by spray drying).

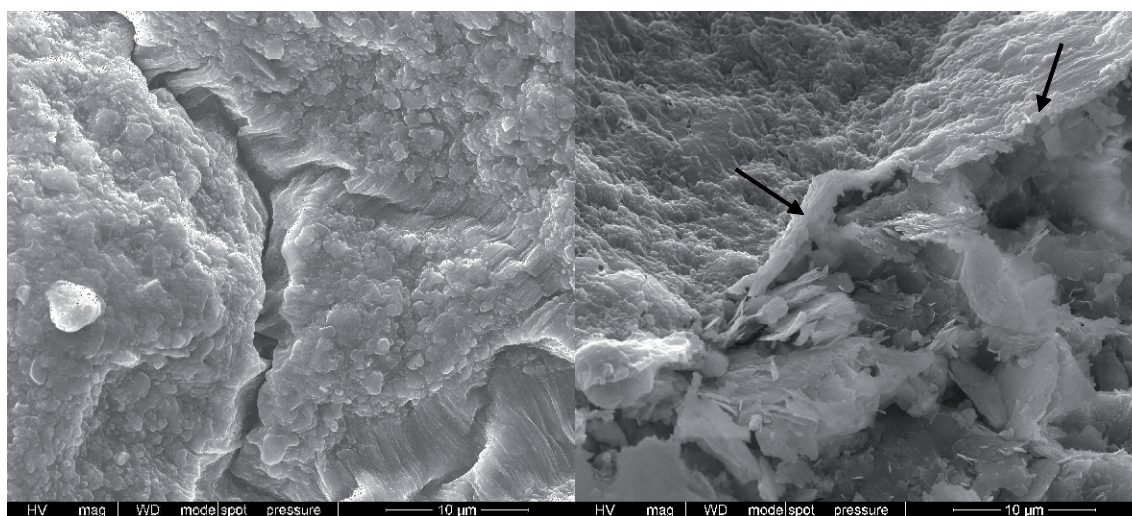


Figure 9. Surface appearance of the granules obtained from the porcelain tile suspension with 1% sodium carbonate (left) and with 5% sodium carbonate (right).

Figure 10 shows that the quantity of Na_2O at the surface of the granules (detected by means of energy-dispersive microanalysis in the SEM) increases with the Na_2CO_3 addition. It should be noted that the quantity of Na_2O inside the granules also increases as the Na_2CO_3 addition rises, albeit to a smaller extent than at the surface.

Taking into account the sodium carbonate deflocculation mechanism, according to the description in the literature [9][13], there must be an ion exchange with the clay in which a part of the Na^+ cations provided by the sodium carbonate are fixed at the clay surface.

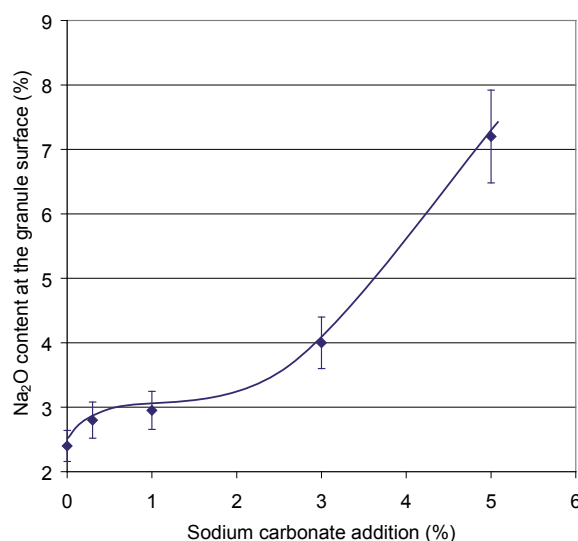


Figure 10. Variation of the quantity of Na_2O at the surface of the granules with the Na_2CO_3 addition (spray-dried powder granules and granules obtained in the laboratory from the porcelain tile suspension).

The carbonate anions will thus precipitate, forming the different sodium carbonate or other carbonate phases, since the suspension contains other cations in addition to Na^+ , as a result of its preparation with well water (on an industrial scale) or water from the mains (on a pilot scale), as well as by the ion exchange that occurs between the clay and the Na^+ cations provided by sodium carbonate. As may be observed in table 5 [14], the solubility of the different carbonates that can form is even lower (with the exception of potassium carbonate) than that of sodium carbonate, which indicates that its precipitation must be favoured. This crystallisation occurs during drop drying, which is why it is reasonable that there should be a greater concentration at the granule surface. Thus, these crystalline phases must establish solid bridges between the clay particles, initially inside the granule during spray drying, and then between the granules during pressing and tile drying. These solid bridges must, therefore, be responsible for the increase in tile mechanical strength since, as it has been previously established, they are one of the most powerful bonding mechanisms that exist [6].

Compound	Solubility (g/100 g H ₂ O)	Temperature (°C)
Na ₂ CO ₃	30.7	25
K ₂ CO ₃	111	25
MgCO ₃	0.18	20
CaCO ₃	0.00066	20
BaCO ₃	0.0014	20
ZnCO ₃	0.000091	20

Table 5. Solubility of different carbonates [14].

4. CONCLUSIONS

The use of sodium carbonate in ceramic tile body compositions increases the mechanical strength of the pressed bodies. This increase in mechanical strength is due to the formation of solid bridges caused by the precipitation of alkaline carbonates and alkaline earths.

It has been observed that there is an optimum percentage of the sodium carbonate addition for each composition at which dry mechanical strength increases without impairing deflocculation behaviour. Additions larger than this optimum percentage, which depends on the composition, lead to greater increases in mechanical strength but they hinder deflocculation owing to the rise in the ionic force of the medium. These results are currently being patented (patent application ° P200930148).

The increased mechanical strength can allow the thickness of the tile bodies to be reduced or larger tiles to be produced. It is also considered to be of great usefulness for porcelain tile compositions with which spray-dried powders intended for dry colouring are obtained.

The possibility of reducing tile thickness entails decreased consumption of resources (water, raw materials, and energy), with the ensuing reduction in costs associated with raw materials, energy, and transport, as well as greater productivity of the facilities.

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