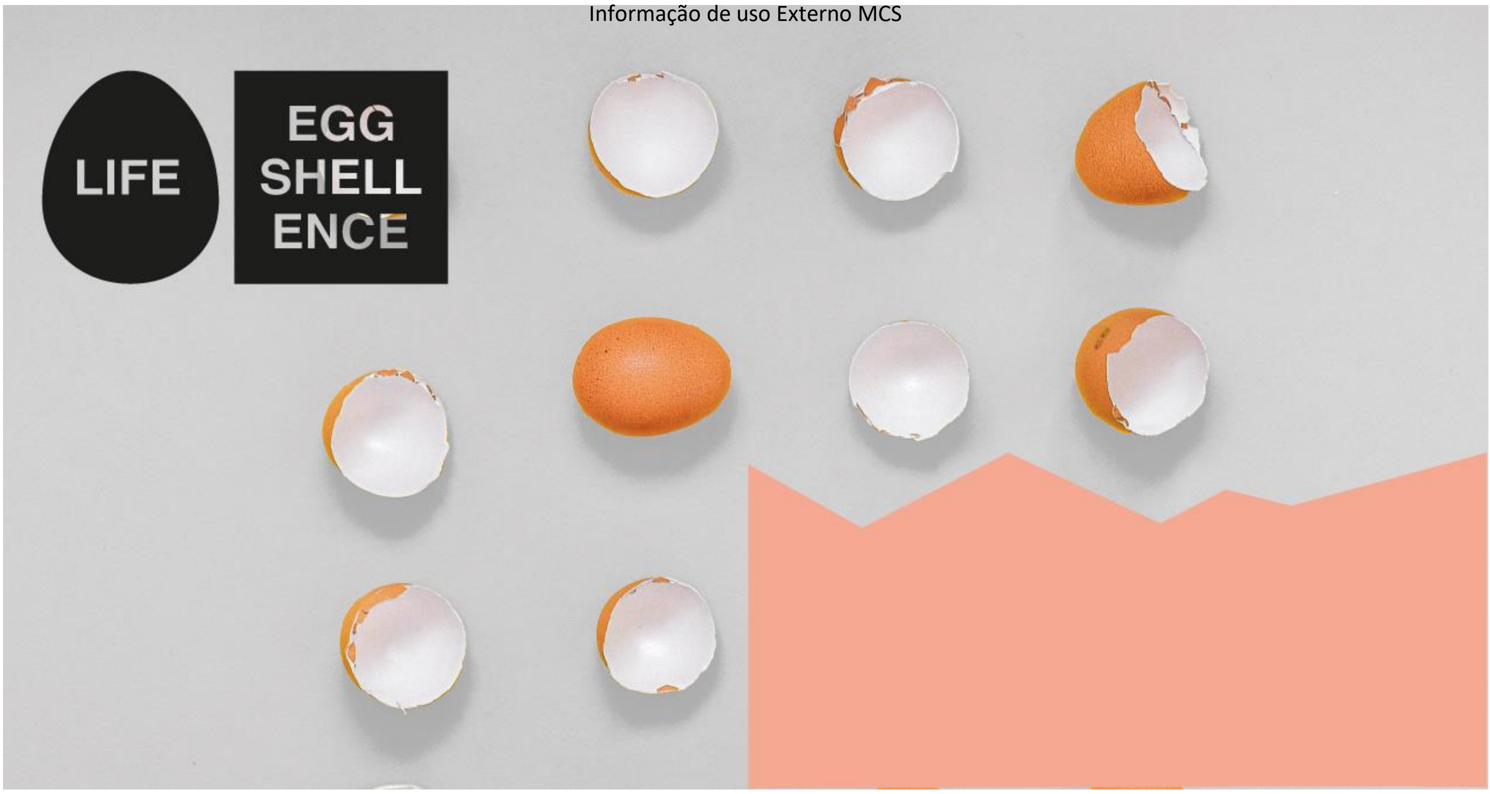

DB2.2.1 Report of the characterization of the spray-dried powders and tiles obtained at pilot scale

This project is financed by the LIFE Programme 2014-2020 of the European Union for the Environment and Climate Action under the project number LIFE19 ENV/ES/000121.
Este proyecto está financiado por el Programa LIFE 2014-2020 de Medio Ambiente y Acción por el Clima de la Unión Europea con referencia LIFE19 ENV/ES/000121.

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1. Introduction

The actions contemplated in the LIFE EGGSHELLENCE project are structured in five groups of actions, being those of type "B" the Implementation actions of the project. This deliverable corresponds to Action B2 "Pre-industrial scale tests of ceramic wall tiles production with eggshell" and describes the results obtained by EATOMIZADO and ADM, with the help of ITC-AICE and UA, in the preparation and characterization of wall tile compositions with bio-$CaCO_3$ at pilot scale. The bio-$CaCO_3$ used in these trials has been provided by AGOTZAINA by processing eggshell in the prototype already installed by MAINCER in its facilities.

In the following sections, the different compositions and the results obtained in their characterization are detailed and commented.

2. Spanish compositions developed by EATOMIZADO

2.1. Initial tests

500 kg of bio-$CaCO_3$ were supplied by AGOTZAINA and 2.5 tonnes of spray-dried powder were obtained. In this trial the bio-$CaCO_3$ was introduced in partial substitution of the mineral calcium carbonate as laboratory tests showed that total substitution could increase substantially the viscosity of the slurry, the tendency to black core formation and also could cause defects on the glazed tiles. The percentage used was 5% (approximately 1/3 of total carbonates content, 14%) and no previous milling of the bio-$CaCO_3$ was performed. The standard composition with 100% mineral calcium carbonate was also processed in order to have comparable results.

The milling of the two compositions was performed in a discontinuous mill of 3 tn in EATOMIZADO facilities (Figure 1).

STD composition was firstly processed (150 minutes of milling time) and the resulting slurry had adequate viscosity to be discharged and spray-dried (25 seconds in Ford Cup, standard device for the control of viscosity at industrial scale). Secondly, the mill was load with the composition with 5% of bio-$CaCO_3$ and after 45 minutes of milling the viscosity was too high (50 seconds). In order to reduce the viscosity, a higher proportion of deflocculant was added in the mill and the milling processed for other 45 minutes. At this point viscosity was 35 seconds, which was considered acceptable and the milling continued until reaching total milling time (150 minutes) with almost no variation in viscosity. This slurry was discarded because of the discontinuous milling and a new slurry was obtained with the new deflocculant addition from the beginning.

Figure 1. Discontinuous mil.

The two slurries were spray-dried (Figure 2) and the resulting powders (Figure 3) were characterized by determining their behaviour in the pressing and firing stages, the content of organic carbon and the tendency to black core formation, their characteristic properties (moisture expansion, thermal expansion, mechanical strength) and key parameters related to the use of bio-$CaCO_3$ without previous milling: the contents of carbonates of high particle size.

Figure 2. Spray-drier used in these tests.

Figure 3. Spray-dried powder obtained.

Table 1 shows the results of particle size distribution, which are very similar for the two compositions and the contents of total carbonates, slightly higher in the STD composition (PATRON REV2009), which must be related more to differences in the load of raw materials in the mill than to the use of the bio-$CaCO_3$ (with 96% of carbonates content, very similar to mineral calcium carbonate, 99%). The main differences are related to the contents of carbonates of high particle size, which again confirm that the milling used is not capable of reducing the bio-$CaCO_3$ particles to sizes below 63 µm (as it is the case of the STD composition due to the use of micronized mineral calcium carbonate). Finally, plasticity is somewhat higher in the composition with bio-$CaCO_3$ because although the same clays and in the same percentages are used (and these are the main factors influencing plasticity), some increase was expected due to the presumable increase in organic matter (typical phenomena observed in clays with high percentages of organic carbon). However, the determination of organic carbon showed no increase, which was not expected because bio-$CaCO_3$ had 1.1% of organic carbon (Deliverable DB1.2.2), and it is used in a percentage of 5% in the spray-dried powder, so there should be an increase of 0.05%.

¡Error! No se encuentra el origen de la referencia. shows the results of the determination of the chemical composition of the two spray-dried powders, which are in good agreement with the theoretical formulations (same raw materials except for the introduction of bio-$CaCO_3$ and with the lower content of carbonates of the composition with bio-$CaCO_3$ already commented, that produce a decrease in the CaO content. These results confirm that the dosing of the raw materials has been performed correctly.

Table 1 Results of particle size distribution, contents of total carbonates and of high particle size, plasticity and organic carbon.

Características iniciales	Bio-$CaCO_3$	STD
Rechazo 45µ (%)	**12,0**	**11,8**
Rechazo 63µ (%)	**4,5**	**4,2**
Rechazo 100µ (%)	**0,4**	**0,7**
CaCO3 (%) Rechazo 45µ	**8,1**	**1,0**
CaCO3 (%) Rechazo 63µ	**9,7**	**1,4**
CaCO3 (%) Rechazo 100µ	**11,3**	**3,5**
Carbono Orgánico (%)	**0,19**	**0,18**
$CaCO_3$ (%)	**13,11**	**13,98**
Plasticidad (und)	**20,2**	**19,0**

Pressing behaviour and mechanical strength of the unfired specimens, Table 2, shows the trends already observed in the laboratory testing associated to the use of bio-$CaCO_3$: lower bulk density at constant pressure and therefore, an increase in pressing pressure to reach similar bulk density, although the changes with respect to the standard composition are not considerable. Regarding mechanical strength, the increase when dry bulk density is kept constant is not as high as it was observed at laboratory scale but this is due to the lower content of bio-$CaCO_3$.

Table 2 Pressing behaviour and dry mechanical strength of the two spray-dried powders.

Características de Prensado	Bio-$CaCO_3$	STD
Humedad (%)	**6,09**	**6,03**
Dap (verde). Pesp.200 (Kg/cm^2)	**2,01**	**2,03**
Presión específica (Kg/cm^2)	**240**	**210**
Dap (verde) (gr/cm^3)	**2,04**	**2,04**
RM (seco) (Kg/cm^2) Dapv = 2,04	**36**	**32**
RM (seco) (Kg/cm^2) P=240 (Kg/cm2)		**35**

Regarding firing behaviour and fired properties the following conclusions can be withdrawn with respect to the use of bio-$CaCO_3$:

- ✓ Very similar firing behaviour in terms of shrinkage, water absorption and bulk density.
- ✓ Similar whiteness of the fired specimens.
- ✓ Fired mechanical strength, thermal expansion and moisture expansion are also very similar. This means that similar crystalline phases have been formed in the two compositions during the firing stage.
- ✓ A slightly higher tendency to black core formation which is in good agreement with what was expected by the use of bio-$CaCO_3$.

Figure 4. Fired specimens.

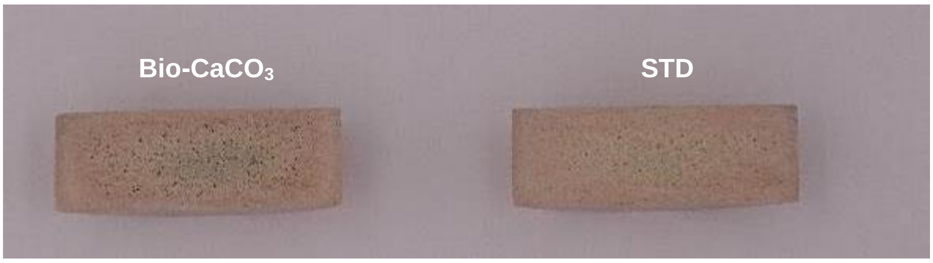

Figure 5. Tendency to black core formation.

To finalize the characterization of the spray-dried powders, 15x15 cm tiles were pressed in ITC-AICE and glazed and fired at industrial scale, and no defects were observed in the glazed surface (Figure 6). This is a very promising result as it would imply that no pre-milling of the bio-$CaCO_3$ is necessary but the small size of the pressed tiles can also help to achieve a perfect glazed surface. So, laboratory firings with shorter firing programs with respect to that used at industrial scale were performed. Typically, wall tiles are fired with firing programs characterized by slow heating in the interval 900-975ºC in order to achieve total decomposition of the carbonates prior to the sealing of the glaze (later decomposition would cause pinholes in the glaze) and higher rates in the rest of the heating. Then, at laboratory scale the heating rate in this interval was progressively incremented until it caused pinholing in the glaze both with the STD composition and with the composition with bio-$CaCO_3$. The results, detailed in Table 3, show a slightly higher tendency to the forming of pinholes in the composition bio-$CaCO_3$ but it is not considered highly worrying. Of course, this has to be confirmed in industrial trials and additionally, a second trial with milled bio-$CaCO_3$ was planned in order to ensure that with similar particle size with respect to mineral calcium carbonates, the tendency to cause pinholes is the same than in STD composition. This second trial is explained in the following section of this deliverable.

Bio-$CaCO_3$ *STD*

Figure 6. 15x15 cm tiles glazed and fired at industrial scale.

Table 3 Presence or absence of pinholes in the glazed surface for different heating rates tested at laboratory scale.

Heating rate in the interval 900-975ºC (ºC/min)	Bio-$CaCO_3$	STD
10	NO PINHOLE	NO PINHOLE
15	SOME PINHOLES	NO PINHOLE
20	MANY PINHOLES	SOME PINHOLES

2.2. Second testing

A second trial was performed but with previously milled bio-$CaCO_3$. A pendulum mill of the pilot plant of ITC-AICE was used, adjusting operation variables to those adequate to reach a reject on 63 µm sieve below 5%. Final variables are listed in Table 10.

Figure 7. Pendulum mill.

Table 4 Operation variables used in the pendulum mill.

Aspiration (Hz)	40/45
Separator (Hz)	50/45
Milling (Hz)	37
Reject on 63 µm sieve of the bio-$CaCO_3$ (%)	4.6

Once milled the bio-$CaCO_3$, the same compositions used in the previous trial were prepared, with identical process variables with respect to the milling and spray-drying operations.

Table 5 shows the results of particle size distribution and the contents of total carbonates, which are very similar for the two compositions. The main differences are related to the contents of carbonates of high particle size, which are still higher in the composition with bio-$CaCO_3$ particles, although not in a considerable proportion. In contrast to the previous trial, in this case plasticity is similar in the two compositions and the determination of organic carbon shows an increase of 0.06%, closed to that expected (in fact the difference could be associated to the uncertainty of the test).

Table 5 Results of particle size distribution, contents of total carbonates and of high particle size, plasticity and organic carbon.

Características iniciales	Bio-$CaCO_3$	STD
Rechazo 45µ (%)	9,96	10,46
$CaCO_3$ (%)	12,50	12,53
CaCO3 (%) Rechazo 45µ	3,65	0,92
Carbono Orgánico (%)	0,15	0,09
Plasticidad (und)	18	18

Pressing behaviour and mechanical strength of the unfired specimens were very similar for the two spray-dried powders. This could be associated to the pre-milling of the bio-$CaCO_3$, aspect to be confirmed in the industrial trials.

Regarding firing behaviour and fired properties, similar conclusions with respect to the previous trial can be withdrawn:

- ✓ Very similar firing behaviour in terms of shrinkage, water absorption and bulk density.
- ✓ Similar whiteness of the fired specimens.
- ✓ Fired mechanical strength is also very similar.
- ✓ A slightly higher tendency to black core formation, similar increase with respect to the previous trial.

To finalize the characterization of the spray-dried powders, 15x15 cm tiles were again pressed in ITC-AICE and glazed and fired at industrial scale, and as expected, no defects were observed in the glazed surface (Figure 10). The results at laboratory scale progressively incrementing the heating rate, detailed in Table 6, show a similar tendency to the forming of pinholes in the composition bio-$CaCO_3$ as was to be expected because of the previous milling of the bio-$CaCO_3$.

Figure 8. Fired specimens.

Figure 9. Tendency to black core formation.

Bio-$CaCO_3$ *STD*

Figure 10. 15x15 cm tiles glazed and fired at industrial scale.

Table 6 Presence or absence of pinholes in the glazed surface for different heating rates tested at laboratory scale.

Heating rate in the interval 900-975ºC (ºC/min)	Bio-$CaCO_3$	STD
10	NO PINHOLE	NO PINHOLE
15	NO PINHOLE	NO PINHOLE
20	SOME PINHOLES	SOME PINHOLES

These two trials confirm the type of trials to be carried out at industrial scale in EATOMIZADO in Action B3:

- ✓ A trial in which bio-$CaCO_3$ will be introduced in a percentage of 5% (as in these pilot trials) without pre-milling. This will help to confirm, this time under real testing conditions with industrial milling, if the bio-$CaCO_3$ can reach the required particle size in the standard milling or if a previous milling is necessary. It will also help to confirm with large format tiles if there is any pinholing (it may happen that although not reaching the required particle size no defects appear in the glazed surface). And of course, the absence of black core will also be checked.
- ✓ The same trial but with bio-$CaCO_3$ previously milled, as it is better to run the two trials in parallel.

3. Portuguese compositions prepared by ADM

Two test phases have been conducted, with standard and full calcite replacement in the first phase and standard and progressive 50, 75 and 100% replacement in the second phase.

As for the procedure, for the batch mills, the eggshell was loaded with the original size (as well as the mineral calcite) and the slip residue was controlled until achieving STD values. It has been observed that the higher the percentage of eggshell, the longer the grinding time.

The two slurries were spray-dried and the resulting powders were characterized.

Figure 11. Fired specimens obtained with the spray-dried powders.

The two pastes with bio-$CaCO_3$ and the STD paste for comparison in production were tested in an industrial 20x30 format, in a tile company.

Figure 12. Fired specimens obtained with the spray-dried powders.

The material was pressed at 280 kg/cm^2 and dried in a horizontal dryer, fired at 1050ºC ring temperature with a 52-minute cycle.
The process characteristics were controlled, obtaining identical results.
The water absorption and mechanical resistance of the final product were controlled, Table 29. The glazing and warping results were similar and approved by production.

Table 28 Properties of industrial tiles.

Refª	%AA	RMC (kg/cm^2)
STD	17.0	210
50% Bio-$CaCO_3$	17.1	209
TOTAL Bio-$CaCO_3$	16.9	210

4. Conclusions

The trials performed allow the following conclusions to be withdrawn:

- ✓ The compositions with bio-$CaCO_3$ require higher percentages of deflocculant or lower solids content with respect to the standard compositions with mineral calcium carbonate in order to achieve the required viscosity for the milling and spray-drying stages, although the differences are not considerable.
- ✓ As already observed at laboratory scale, the behaviour in the pressing and firing stages of the spray-dried powders with bio-$CaCO_3$ are very similar to those of standard compositions. The same thing happens with thermal expansion or chromatic coordinates.
- ✓ As a positive effect, in many of the trials dry mechanical strength is observed to increase with the percentage of substitution of mineral calcium carbonate by bio-$CaCO_3$ confirming the binding properties of the new secondary raw material.
- ✓ Although there is an increase in organic matter, an acceptable tendency to black core formation has been observed in the compositions with 5% of bio-$CaCO_3$ (as in this percentage the increase in organic carbon is not too high).
- ✓ In order not to have defects in the glazed tiles associated to the decomposition of carbonates of high particle size (when bio-$CaCO_3$ is used without previous milling), the optimum firing cycle is a bit longer with respect to the use of pre-milled bio-$CaCO_3$. This aspect has to be confirmed in the industrial trials of Action B3.