PHASE CHANGE MATERIALS INTEGRATED INTO GLASS SCRAP-BASED TILES FOR VENTILATED FAÇADE APPLICATIONS: A LABORATORY SCALE-UP CASE STUDY

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1. ABSTRACT

Ceramic foams represent an interesting class of materials for applications as insulators, thanks to their low flammability, which makes them a safer alternative to polymeric insulation products. Ceramic foams are characterized by peculiar microstructures with a porous texture, whose formation can be induced by the introduction of a foaming agent. Its activation within the ceramic batch is achieved during the firing process. The integration of Phase Change Materials (PCM) into the pores of the ceramic matrix represents a challenging goal to significantly improve the thermal insulating performances and comfort of buildings. The possibility to integrate

PCM into porous fired tiles is strictly related to the size and number of pores formed during the process. For this purpose, the ability to control and predict the bloating phenomena as a function of tile size is a key point in defining the thermal performance of the final device. Starting from a typical porcelain stoneware tile formulation, silicon carbide (SiC) powder was added as foaming agent. Furthermore, the bulk composition was optimized by addition glass scraps, with a view to reducing carbide stability in order to observe bloating phenomena in a temperature range typical of industrial ceramic tile production. To evaluate how tile size can influence microstructure, in terms of amount, shape and size of pores, a laboratory scale-up process was carried out. It was done by going from small specimens (30 mm in diameter) to a demonstrator device (150x150 mm). The samples were characterized by bulk density, linear expansion, water absorption and pore distribution. The effects of the firing process parameters on physical properties were studied. The increase in temperature led to an initial decrease in the bulk density, caused by gas formation due to SiC oxidation, followed by a progressive densification regardless of the increased expansion potential. The amount, size and shape of pores are dependent on both the efficiency of SiC decomposition and glass viscosity. The changes in terms of density are consistent with the porosity, affecting the potential amount of PCM that could be incorporated. Linear bloating and pores size showed an evident relationship to the specimen size, emphasized by the reduction of the heating rate.

2. INTRODUCTION

In the last few years buildings have become one of the most energy-consuming sectors, responsible in the European Union for 36% of all CO2 emissions [1]. The transition from traditional structures to Nearly Zero-Energy edifices will enable higher energy effectiveness and decarbonized building stocks. Given the increase in global warming phenomena, urbanization and economic growth of developing countries, the use of energy for indoor cooling is growing faster than other building end uses [2]. Furthermore, the use of energy-intensive cooling devices, like fans and air conditioning installations, contributes significantly to the heat island effect, thus increasing the cooling demand. Among the different technological solutions that can be used to improve thermal comfort, solar thermal energy storage systems, based on Phase Change Materials (PCM) can play an important role. As a result of the high energy storage density, obtained for latent heat-based systems, it is possible to reduce the gap between energy demand and supply, by shifting the peak load to the off-peak hours, thus damping global consumption [3-4].

The effect of the PCM incorporation within the building envelope was already studied [5-7]. Organic materials, like paraffins and fatty acids, present several advantages, like no solidification subcooling, low hysteresis and higher stability with respect to inorganic compounds, such as salt hydrates [8]. The low thermal conductivity of these materials, which may reduce heat absorption, can be overcome by their optimized integration within a defined structure. To ensure full solidification during warmer seasons, the implementation into ventilated façades can be done [9-11]. The integration into insulating envelopes allowed combination of the effect of sensible and latent heat, improving thermal performances. The incorporation of PCM can be achieved by different mechanisms, like direct incorporation [12-13], immersion [14] encapsulation [6-15-16] and shape stabilization [17]. Cement, mortars and perforated bricks are the most widely studied materials, since PCM can be integrated without firing treatment [7-18-20]. On the other hand, studies considering the use of PCM in porous tiles are rather scarce [21]. Among the possibilities mentioned, only the immersion technique can be used to incorporate PCM into a ceramic porous structure [22]. Impregnation under vacuum improves process efficiency [23]. The pore formation in the ceramic matrix can be achieved by adding several additives [24-25]. In particular, the use of a foaming agent leads to obtaining large porosity, useful for PCM storage. Furthermore, the addition of glasses enhances bloating phenomena [26]. Foam production may present problems during the scale-up process in terms of predictability of bloating and shape stability. The connection between process parameters, mostly the device size, on the observed expansion and final properties is still missing. The goal of this work was to obtain PCM-containing lightweight ceramic tiles for ventilated façades. The effect of scale-up on ceramic foam properties was evaluated. Furthermore, effects on the PCM incorporation efficiency and thermal properties were appraised.

3. EXPERIMENTAL

The formulations studied were obtained by dry mixing of additional components to a commercial porcelain stoneware spray-dried powder. Given its possible occurrence in ceramic polishing sludges (as a result of lapping tool abrasion) and the interest in the introduction of wastes into the production process, silicon carbide was selected as expanding agent. The batches were tested in order to optimize bloating in a typical ceramic production temperature range.

In particular, glass scraps were added in order to reduce SiC stability, lowering oxidation temperature. Solid urban waste glass scraps, previously crushed and sieved to particle size lower than 100μm, were selected. Furthermore, dolomite was added to improve bloating. The chemical composition of the materials is reported in table 1. The selected formulations are reported in table 2.

Samples were formed by uniaxial pressure up to 150kg/cm^2 using two different laboratory hydraulic presses. In order to favor particle adhesion during molding, 6wt% of PEG was added to the powder mixtures. Circular specimens were pressed with a standard laboratory press (Nannetti) using 30 mm and 60 mm diameter molds. Rectangular and squared ones were obtained using a customized laboratory press (Giuliani) using 115mmx120mm and 150mmx150mm molds.

Shaped samples were dried at 120°C for 8h, then fired in a temperature range from 950 to 1150°C. Two different thermal cycles were set up, in order to control the effect of the firing condition on bloating phenomena. Rapid firing cycle, in order to simulate the industrial firing process with a thermal gradient of 40°C/min up to peak temperature that was maintained for 5 min. A slow firing process was achieved using a heating rate of 2.5°C/min to maximum temperature, without soaking time. In both cases an electric kiln was used.

Fired specimens were characterized for water absorption, total porosity, bulk density (ISO 10545-3 for 3cm specimens – geometric density for scaled-up ones) and linear bloating (as $100\cdot(Lf-L_m)/L_m$, where L_f is the diameter of the fired sample and L_m is the mold diameter).

Microstructures were studied using an OLYMPUS S2X optical microscope, equipped with a Nikon Digital Sight DS-Fi2 camera (5-megapixel CCD, 2560 x 1920 pixels resolution).

Thermal performance was measured by the guarded heat flow meter technique (UNI EN ISO 10456) on rectified specimens with a diameter of 50.8±0.25 mm and thickness of 7.5mm.

An organic bio based commercial Phase Change Material (PCM) was selected, characterized by a melting temperature of 29°C and a melting latent heat of 207 kJ/kg.

Foam impregnations were carried out under vacuum condition in a glass crystallizer. Fused PCM was maintained at 30°C using a hot plate. Rectified samples were impregnated by direct immersion in melted PCM for 30min. After impregnation, the excess PCM was removed.

wt%	Stoneware powder	Glass scraps
SiO_2	73.41	71.70
TiO_2	0.67	0.07
Al_2O_3	17.08	2.70
Fe_2O_3	1.47	0.42
MgO	0.51	2.00
CaO	0.99	9.49
Na_2O	3.37	12.40
K_2O	1.94	1.01

Table 1 *Chemical composition of tested materials*

Raw materials (wt%)	Sample A	Sample B
Stoneware powder	49	39
SiC	1	1
Dolomite	-	10
Glass scraps	50	50

Table 2 *Formulation of experimental bodies.*

4. RESULTS AND DISCUSSION

Foam optimization

In order to understand the effect of the composition on bloating, batches A and B were both fired in the 950-1150°C range, using a rapid firing cycle, mimicking the industrial process. The macro and microstructure of the materials undergo important changes within the range studied (Figure 1). At 950 °C, both formulations show a limited bloating, characterized by the presence of small pores with a diameter of about 1 mm. The addition of dolomite, in batch B, favors the formation of bigger pores characterized by irregular shape and diameter between 1 and 5 mm. Furthermore, the sample cross section shows a lower deformation. The micrographs show that the spray dried powders act as refractory elements, reacting to a limited extent with the glassy phase, which instead is involved in the bloating phenomena. The dissolution of SiC into the viscous phase promotes carbide oxidation and pore formation. Regardless of the carbide effective oxidation efficiency, the bloating is limited by gas leakage through the porous structures. In specimens fired at 1150°C a general increase in pore size is observed. Specimen A exhibits a main porous structure characterized by pores with diameters that reach 15 mm, and a secondary porosity formed by pores present within the septa, with diameters lower than 1.5 mm. Also in this case, the addition of dolomite, in batch B, enhances specimen bloating [27]. The pore size is significantly increased by carbonate decomposition, with the formation of pores with diameters reaching 30 mm. As a result of higher expansion, septa appear thinner, with holes generated by secondary porosity opening. The increase in temperature lowers the glassy phase viscosity and gives rise to an improved stoneware particles dissolution. These two combined effects induce a progressive structural collapse, limiting gas holding and increasing bulk density.

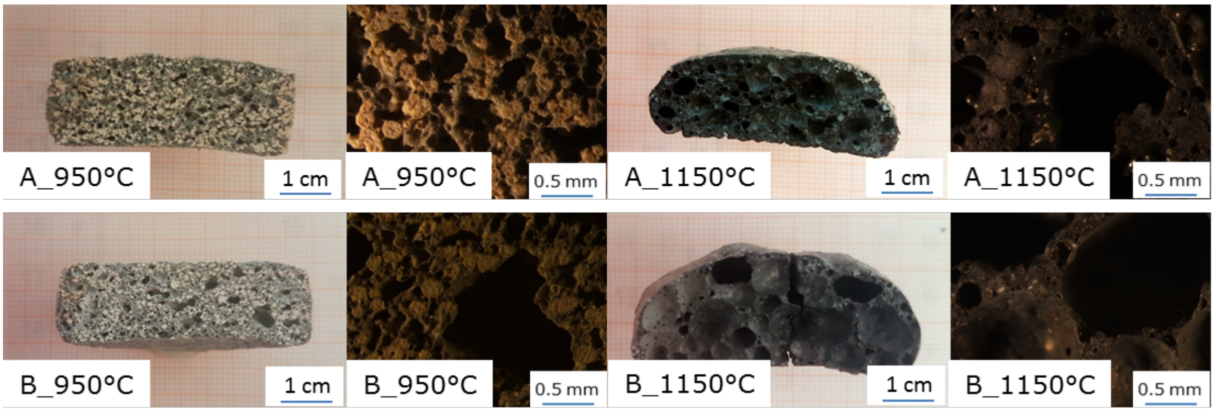

Figure 1 *Effect of firing temperature on macro and microstructure; A and B 3-cm samples – slow firing cycle.*

The trend displayed by bulk density as a function of firing temperature is reported in Figure 2. The minimum value is observed at different temperatures: for A formulation, bloating is observed at 1000°C. Further temperature rise increases the bulk density. The addition of dolomite gives rise to a secondary bloating. Dolomite decomposition, favored by the increase in temperature, brings about a further expansion and a maximum bloating at 1075°C. The progressive decomposition of SiC and dolomite boosted the gas pressure in the specimens, favoring gas leaking and development of open pores. Pore size distribution strongly depends on the properties of the glassy phase during the firing process. Furthermore, the decrease in viscosity and surface tension, given by temperature rise, yields an increase in the bubble size and coalescence. In accordance with the minimum density, sample A shows a pore size distribution in the 1-4 mm range. In the B mixture, larger pores are observed, between 1 and 8 mm.

In addition to temperature, the firing cycle plays a key role in determining the foam properties. To evaluate this aspect, both batches A and B were fired using a slower heating rate. Table 3 reports the effects in terms of physical properties change. It may be noted that bloating phenomena are importantly enhanced. The increase in heating time favors both carbide decomposition and pores expansion, giving rise to a bulk density reduction. As firing temperature is the same, the melt viscosity is not modified, and the pore size distribution is not significantly modified. This phenomenon is more evident in case of A specimens, however obtaining higher density values.

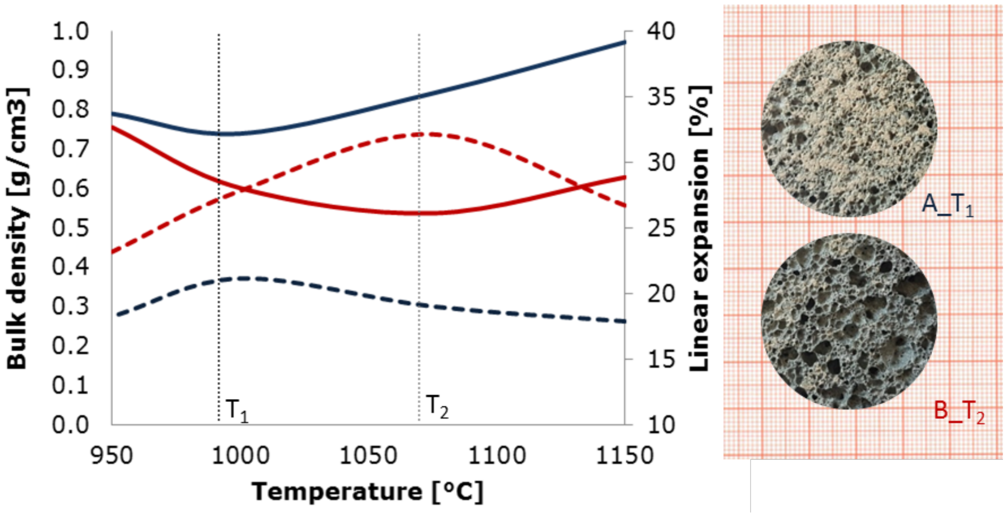

***Figure 2** Effect of composition and firing temperature on 3 cm specimen properties (Full lines: bulk density - Dashed lines: linear expansion – Blue lines: A formulation - Red lines: B formulation).*

Percentage changes of physical properties (%)	Sample A	Sample B
ΔLinear expansion	48	36
ΔWater absorption	32	30
ΔBulk density	-51	-43
ΔTotal porosity	12	11

***Table 3** Changes in physical properties for A and B batches fired at 1075°C: heating rate 40°C/min versus 2.5°C/min. Values expressed as percentage of the fast cycle figure.*

PCM-containing foam scale-up

In order to enhance the foam performances, in scaled-up lightweight material production, the process parameters were defined and set up. The thermal properties of the foam depend on both pore amount and morphology. At the same time, the properties of the final composite system are strongly related to the amount of PCM incorporated within the porous structure. The impregnation efficiency is strictly related to the foam properties. In order to establish the effect of firing cycle parameters on the amount of PCM that can be incorporated, samples fired at 1075 °C and 1150°C (rapid and slow cycles) were tested. Regardless of the higher foam bulk density of specimens fired at 1150 °C, the effect of larger pores was assessed.

Rectified specimens were impregnated and the amount of PCM incorporated was defined in terms of volume percentage. The results obtained, reported in Figure 3, show different trends. For both formulations, the increase in firing temperature gives rise to a lower volume of incorporated PCM. The progressive densification of the material, driven by improved viscous flow, reduces the porosity, limiting the maximum impregnation achieved. At the same time, the formation of larger pores, opened during the rectification process, lowers the ability to retain fused PCM, contrary to what was expected, in case of A formulation (Figure 3).

Figure 3A shows the reduction of heating rate brings a lower impregnation efficiency. Regardless of the increased bloating, the pores formed cannot be filled under the impregnation condition used in the present study. In contrast, for the B specimens the lowering of the heating rate increased the efficiency observed, which is higher also when compared to the corresponding A sample.

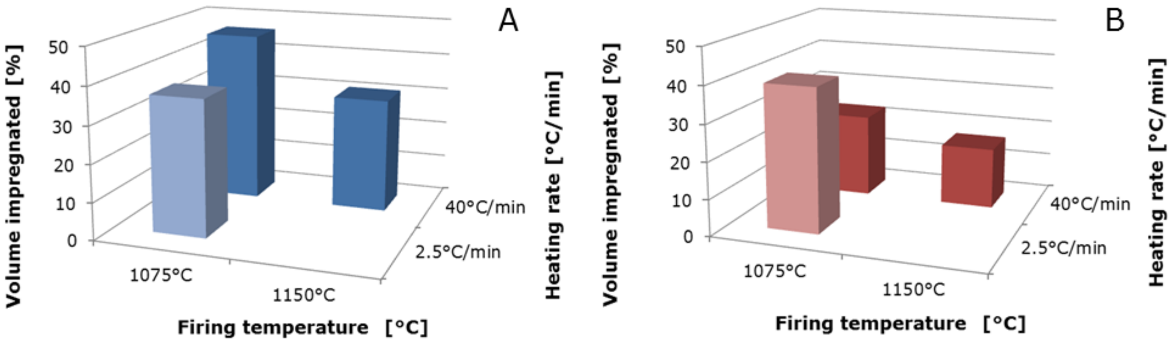

***Figure 3** Effect of firing parameters on impregnation efficiency for A and B formulation*

The addition of PCM to the ceramic foams modifies the insulation properties. The substitution of PCM after air gives rise to an increase in thermal conductivity. Thermal performances measured, reported in Figure 4, show different trends. The foam thermal conductivity undergoes a linear increase with the rise of bulk density (Figure 4A). After impregnation, a deviation from the linearity is observed. In any event, the B samples maintain more stable values, also for the PCM-richer sample. A more evident effect of the foam properties on thermal properties can be seen considering the change in conductivity (Δλ) as a function of the bulk density increase (Δρ) measured for each sample (Figure 4B). While in batch A, it remains quite constant, the B specimens show a progressive increase in Δλ.

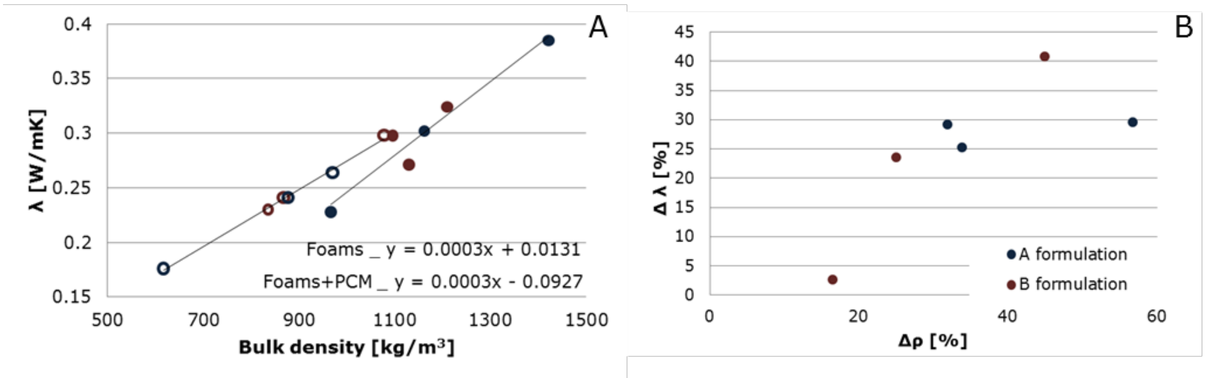

***Figure 4** Thermal conductivity: A) Rectified foams - o: Foam - •: Foam +PCM – Blue circles: A samples - Red circles: B samples. B) Effect of foam properties on measured conductivities.*

The optimal conditions for scale-up were defined starting from the results obtained in terms of foam bulk density, impregnation efficiency and thermal conductivity. Considering its lower bulk density and thermal conductivity, which remain unchanged within the range studied, the B formulation was selected. Given the higher impregnation efficiency achieved, the firing cycle was set at 1075°C with a heating rate of 150 °C/h.

Firstly, the scale-up process affects bloating and specimen properties (Table 4). Regardless of the effect of press change, the trend of fired sample properties is still observed. In particular, the increase in specimen size gives rise to a lower bloating. We can thus assume that the higher weight raises the capillary pressure limiting pore expansion.

The effect of specimen size on impregnation efficiency is reported in Figure 5. In this case, the pore amount seems to affect less the amount of PCM incorporated. Impregnation efficiency is affected by sample dimension to only a small extent. In fact, it may be noted that a volume increase of about 1500% leads to a reduction of impregnated volume of only 15%. No changes are observed for the sample.

Mold size [mm]	Bulk density [g/cm^3]	Total porosity [v/v%]
Ø30mm	0.35	86
Ø60mm	0.51	69
115x120mm	0.39	85
150x150mm	0.46	82

***Table 4** Effect of scale-up on fired specimen properties.*

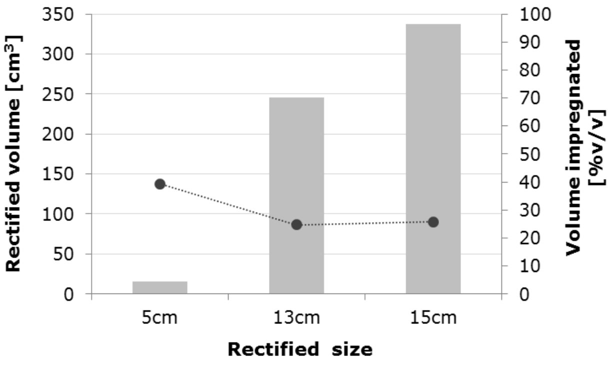

***Figure 5**. Effect of specimen size on impregnation efficiency of rectified samples (Bars: Rectified volume – Dots: Volume impregnated)*

5. CONCLUSIONS

The production of ceramic foam, by a process mimicking tile production presents several drawbacks intrinsically linked to the porous structure formation mechanism. In particular, control of the gas formed by SiC oxidation is a challenging target made more difficult by the change in product size during scale-up. The capillary pressure inside the formed bubbles is also affected by the weight of product. The composition and firing optimization enabled achievement of a lightweight ceramic foam involving the use of wastes. The scale-up study showed a progressive reduction of firing expansion resulting from increased product size. At the same time, a small effect on impregnation efficiency was observed.

Future work will be focused on the evaluation of composite performances as insulation element in ventilated facades.

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