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Campanian Ignimbrite as raw material for lightweight aggregates

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Abstract

Aim of this research is an evaluation of the zeolitized facies of Campanian Ignimbrite as raw material for the production of lightweight expanded aggregates (LEA). A commercial product (Cab70) was used as reference for this rock. Tests were carried out on "pure" samples or mixed with an industrial waste mud (DPM — Dried Polishing Mud) deriving from a porcelain stoneware tile polishing process. This mud contains SiC, a phase known to act as bloating enhancer. Raw materials were subjected to mineralogical (XRPD–RIR method) and chemical (XRF) analyses. Bloating upon heating was measured (Leitz heating microscope) on Cab70, DPM and on three mixtures having the following Cab70/DPM ratios: 85/15 (Mix1); 70/30 (Mix2); 50/50 (Mix3). LEA production was assessed both in static (muffle kiln) and in dynamic (rotating kiln) conditions by firing pellets, 3–8 mm in size, between 1220–1380 °C. The unit weight of the single particle was determined on fired and unfired products. All materials evidenced a decreasing density with temperature whereas the same parameter decreases with DPM increasing content. Cab70 LEAs never dropped below 0.90 g/cm^3, even at the highest temperature, whereas DPM LEAs range between 0.86 g/cm^3 (at 1260 °C) and 0.46 g/cm^3 (at 1380 °C). A direct but not linear relationship between DPM content and density was evidenced. Among the three mixtures, Mix2 showed the lowest DPM content able to produce the strongest density reduction. To get LEAs with the same density the rotating kiln required temperatures generally 60–80 °C higher than those of the muffle kiln. This difference should be related to the different thermal insulation of the two systems during firing. Two sets of LEAs were massively produced in dynamic conditions from Cab70 (at 1380 °C) and Mix2 (at 1300 °C). These latter showed better technical performances in terms of unit weight of the single particle (0.81 vs. 0.98 g/cm^3), bulk unit weight (460 vs. 565 kg/m^3), water absorption coefficients (1.4 vs. 5.5% after 24 h) and compressive strength of the particles (2.9 vs. 0.6 MPa). Differences in pore shape, dimension, abundance and spatial distribution were observed by SEM between the two sets. The technical features of these LEAs were comparable to some expanded clays, with similar grain size, commercialised in Italy.

These results are worth interesting as they reveal new perspectives of application both for a rock characterized by a low exploitation cost and widely available in central-southern Italy, as well as for an industrial waste produced in high amount but not recycled at all.

Keywords: Aggregates; Waste; Campanian Ignimbrite; Zeolite; Porcelain stoneware

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1. Introduction

Aggregates are natural or artificial cohesionless materials constituted by elements with different grain size. According to UNI EN 13055-1 (2003) definition, "lightweight aggregates" need to satisfy two requirements: i) a mass/volume ratio not higher than 2000 kg/m^3 for each single particle; ii) a bulk unit weight not higher than 1200 kg/m^3. The main parameter that distinguishes "lightweight aggregates" from "dense aggregates" is the bulk unit weight (Klinefelter, 1960; Dower, 1987; Loughbrough, 1991). The lightweight aggregates are used as loose material — for example in back wall fillers and in agronomic applications — or, with a binder, in the manufacture of plaster, asphalt and lightweight concrete thermo-acoustic insulators, as well as in lightweight structural concrete production.

Lightweight expanded aggregates (hereafter LEA) can be formed by a quick heating at high temperature of some rocks which are able to bloat. Usually, they are industrially produced starting from clay or shale. The raw material must contain substances that develop gas upon heating and, at the same time, the material must transform into a highly viscous plastic mass able to expand by virtue of gas entrapment. The estimated Italian LEAs production is 1 mm^3/year with proceeds of 50 M€ (Zanatta, 2002). In Italy LEAs are currently manufactured using clays (Troli et al., 2002). These are processed in rotating kilns at temperature up to 1300 °C (ANPAE, 2003). The chemical range of composition of clayey rocks able to expand was experimentally defined by Riley (1969). LEAs can be obtained also by using zeolite-rich rocks (Mumpton, 1978). Low density bricks and other utilities were directly prepared with zeolitized rocks (Torii, 1978; Gayoso Blanco et al., 1991; Kazantseva et al., 1996, 1997). Also Italian zeolitized rocks were evaluated in LEAs production (Sistu, 1990; Sistu and Atzeni, 1993; de' Gennaro et al., 2001; de Gennaro et al., 2004). In addition, by using LEAs prepared with Neapolitan Yellow Tuff, a lightweight structural concrete showing physical and mechanical properties comparable to commercial products was obtained (de Gennaro et al., 2005).

Russian researchers have enhanced the expandability of zeolitized rocks by adding small quantities (1–2 wt.%) of silicon carbide (SiC) as bloating agent (Kazantseva et al., 1996, 1997). Due to SiC market price (7.00 to 9.00 €/kg in Italy) its use, even in small quantities, would increase LEA final cost. On the other hand, Italy produces huge amounts of SiC bearing industrial wastes, represented by mud derived from the polishing process of porcelain stoneware tiles. The national agency for environmental protection (ANPA — Agenzia Nazionale per la Protezione dell'Ambiente) of Emilia Romagna region, and the association of Italian ceramic manufacturers (Assopiastrelle) have studied the environmental impact of ceramic industry in the Sassuolo–Scandiano district, where the 80.3% of national tile production was attained already in 1999 (ANPA, 2002). In this sector, during the years 1990–1999 the quantity of dry mud resulting from the polishing process of porcelain stoneware tiles has increased from 13,000 to 46,000 t (Table 1). Also, considering that from 1999 to 2004 the Italian production of porcelain stoneware tiles recorded a growth of 65% (Assopiastrelle, 2000, 2003, 2005) it is reasonably to deem that the quantity of polishing mud has increased too. This waste represents an environmental problem since, at present time, it is not recycled.

Table 1
Quantities of dry mud from porcelain stoneware polishing (DPM) produced between 1990 and 1999 (data from ANPA, 2002)

Year	1990	1992	1994	1996	1997	1998	1999
DPM (kt)	13,319	15,572	21,349	32,331	35,000	42,800	46,000

This research aims at: 1) evaluating the zeolitized facies of Campanian Ignimbrite, a trachytic pyroclastic rock extensively outcropping in Campania (Southern Italy), as an alternative raw material in LEA production, to take advantage from its availability and low cost; 2) testing the use of mud derived from porcelain stoneware tile polishing as a bloating agent for Campanian Ignimbrite in LEA production.

2. Materials and methods

The Campanian Ignimbrite, the most important and widespread pyroclastic formation of Southern Italy (Fisher et al., 1993), was deposited 39,000 years b.p. (De Vivo et al., 2001) as a result of the main explosive activity in the Mediterranean region during the Quaternary (Barberi et al., 1978). This formation is characterized by four stratigraphic units (Cappelletti et al., 2003). One of them, the Lithified Yellow Tuff (LYT), has been deeply affected by a zeolitization process, that brought about a mean zeolite content (phillipsite+chabazite) of about 60 wt.% (Cappelletti et al., 2003). This mineralogical feature promoted the development of potential technological applications in environmental fields, agriculture, zootechny, etc.

The material investigated for the present study, coming from the volcaniclastic formation of Campanian Ignimbrite, has the commercial name of "Cab70" and is traded by an Italian company (Italiana Zeoliti s.r.l.) which exploits a deposit located in Comiziano–Naples. Among the grain size fractions available, the following were used for the experiments: a 3–8 mm granulate (tested without preliminary operations), and a powder <200 μm (employed for pellets preparation — see further).

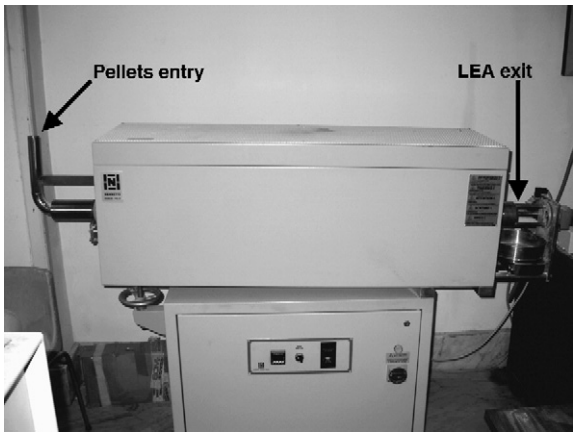

Fig. 1. The rotating kiln used to produce LEA in dynamic conditions.

The industrial waste used in combination with the above described natural products is a dry powdered mud (<200 μm) (hereafter, DPM) deriving from the polishing process of porcelain stoneware tiles produced by a polishing plant located in Sassuolo (Modena). It is classified as an industrial waste by the Italian Law since 1997, as stated in the Official Bulletin of Italian Republic (Suppl. Ord. G.U.R.I., 1997).

Mineralogical quantitative determinations of tested raw materials were performed by X-ray powder diffraction using the reference intensity ratio (RIR) method (Bish and Chipera, 1988); whenever possible, reference standards were separated from investigated rocks. Data were collected using a Philips PW1730/3710 equipped with a curved graphite diffracted-beam monochromator (Cu Kα radiation, 40 kV, 30 mA; 3–80° scanning interval, step size=0.020° 2θ, counting time 10 s per step). Errors for each single phase are based on the standard deviation of the RIR values.

Chemical analyses of raw materials were carried out by XRF (PW1400 Philips equipped with a W tube) at C.I.S.A.G. — Centro Interdipartimentale di Servizio per Analisi Geominer-alogiche, Naples University. Data were corrected for drift and background effects. Data reduction was performed using the methods proposed by Franzini et al. (1972 — major elements) and Leoni and Saitta (1976 — trace elements). Maximum errors are as follows: ±1% for SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, K_2O and MnO; ±4% for MgO, Na_2O and P_2O_5. Maximum errors for trace elements vary according to their concentrations: ±2–3% at 1000 ppm; ±5–10% at 100 ppm; ±10–20% at 10 ppm. Detecting limit is 3 ppm for the majority of measured trace elements. Loss on ignition (L.o.I) was determined by firing samples for 2 h at 1000 °C.

Table 2
Mineralogical composition of Cab70 (wt.%)

Sample	Phi	Chab	Feld	Biotite	Sm	Pyr	Glass
Cab 70	51±2	12±1	20±3	Traces	6±1	Traces	11±6

Phi: Phillipsite; Chab: Chabazite; Feld: Feldspar; Sm: Smectite; Pyr: Pyroxene.

Table 3
Chemical analyses of Cab70 and DPM

Major elements	Cab70 (wt.%)	DPM (ppm)	Trace elements	Cab70 (wt.%)	DPM (ppm)
SiO_2	54.52	64.45	Zn	96	1109
TiO_2	0.45	0.59	Rb	263	304
Al_2O_3	15.19	16.70	Sr	319	554
Fe_2O_3	4.00	0.35	Y	164	41
MnO	0.17	0.02	Zr	390	16320
MgO	0.88	6.21	Nb	57	24
CaO	4.14	1.53	Sc	6	7
Na_2O	1.04	3.82	V	42	49
K_2O	6.98	1.60	Cr	–	477
P_2O_5	0.10	0.05	Cu	3	91
L.o.I.	12.53	4.68	Ba	275	438

Technological characterizations were performed on DPM and Cab70, as well as on the following mixtures (wt.%):

- Mix1=85% Cab70 and 15% DPM;
- Mix2=70% Cab70 and 30% DPM;
- Mix3=50% Cab70 and 50% DPM.

The fusibility tests on Cab70, DPM and the three mixtures were carried out with a Leitz heating microscope. Samples with prismatic shape (square base: 9 mm^2; height: 6–7 mm) were heated at a rate of 10 °C/min until melting was achieved. The deformation of the samples (ε%) upon heating was checked through a series of micrographs taken at temperature steps of 10 °C. This procedure allowed to draw the sintering curves and to define:

- T_s (temperature at which sintering ends): graphically measured, this parameter indicates the lowest volume of the sample during heating.
- T_r (starting softening temperature): evaluated by micro-graph observation when the edges of the specimen loose their sharpness.

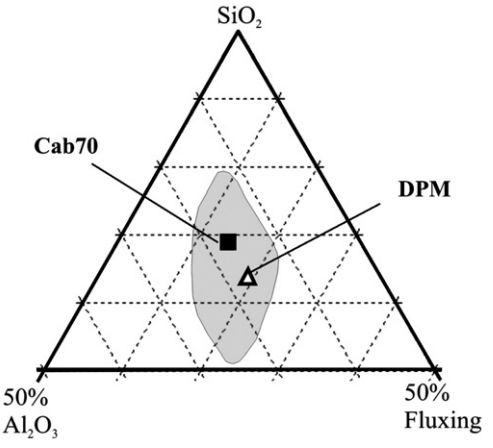

Fig. 2. Cab70 and DPM projected into the Riley diagram: the grey area corresponds to compositions of expanding materials (Riley, 1969).

Table 4
Results of fusibility tests

Sample	T_s	T_r	T_{me}	T_{mve}	T_f
Cab70	1210±10	1240±10	1255±10	1234±10	1340±10
Mix1	1150±10	1230±10	1240±10	1208±10	1350±10
Mix2	1160±10	1220±10	1230±10	1200±10	1350±10
Mix3	1160±10	1220±10	1230±10	1200±10	1340±10
DPM	1140±10	1180±10	1220±10	1183±10	1392±10

Characteristic temperatures (in °C) of: T_s — end of sintering; T_r — starting softening; T_{me} — maximum bloating; T_{mve} — maximum kinetic of bloating; T_f — melting.

- T_{me} (temperature of maximum bloating): graphically measured, provides information of the highest volume reached by the specimen after the T_s.
- T_f (melting temperature): evaluated by micrograph observation when the specimen achieves a hemispheric shape.
- T_{mve} (temperature of maximum bloating kinetic): highest value of $d\varepsilon / dt$ graphically measured using the derivative of the sintering curve.

Once determined the T_{mve} for all the samples, the behavior of the materials at those temperatures was evaluated as a function of time by the following test. Each sample was quickly (14 min) brought to its T_{mve}, and then the temperature was maintained constant for 30 min. During this span of time sample volume variations were monitored, and the relative diagram was accomplished. Volume variations were normalized to the starting volume.

LEA production was assessed both in static (Controls muffle kiln) and in dynamic (Nannetti rotating kiln: mod. TO-

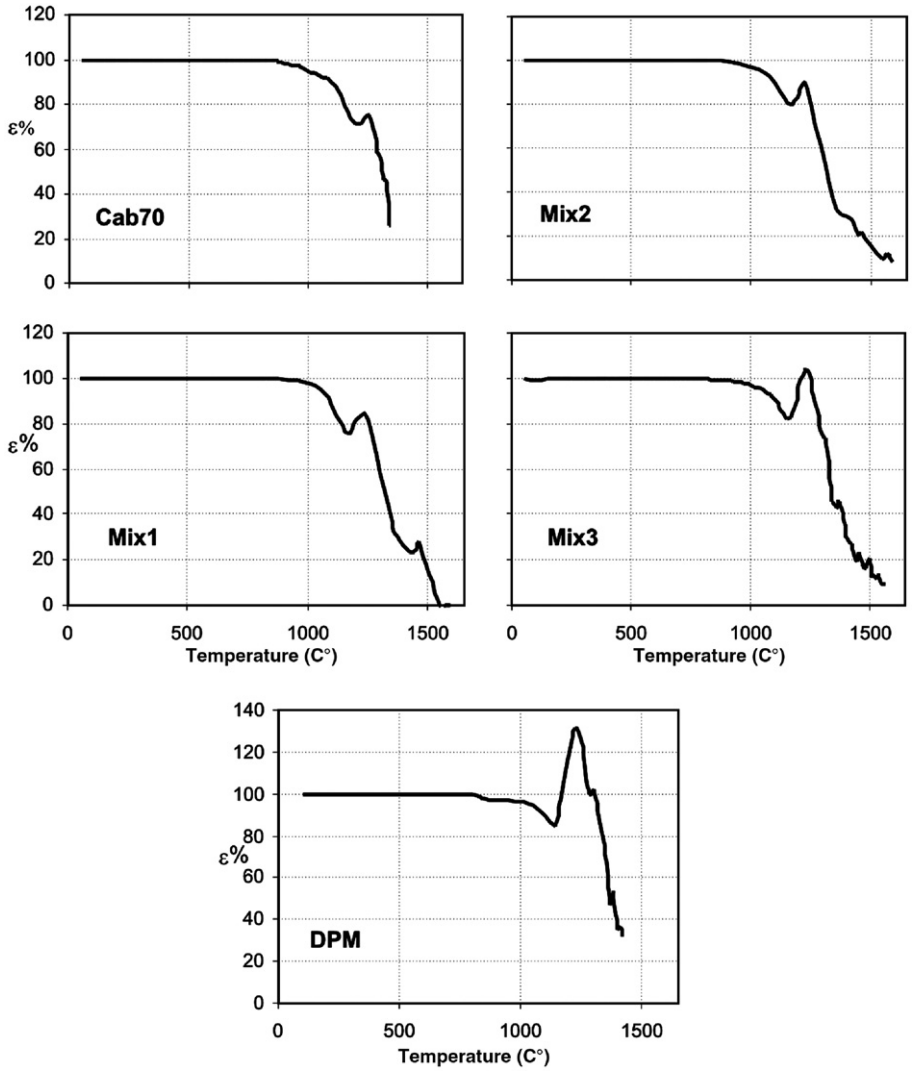

Fig. 3. Sintering curves. ε% represents sample height referred to the initial height (100% corresponds to undeformed samples).

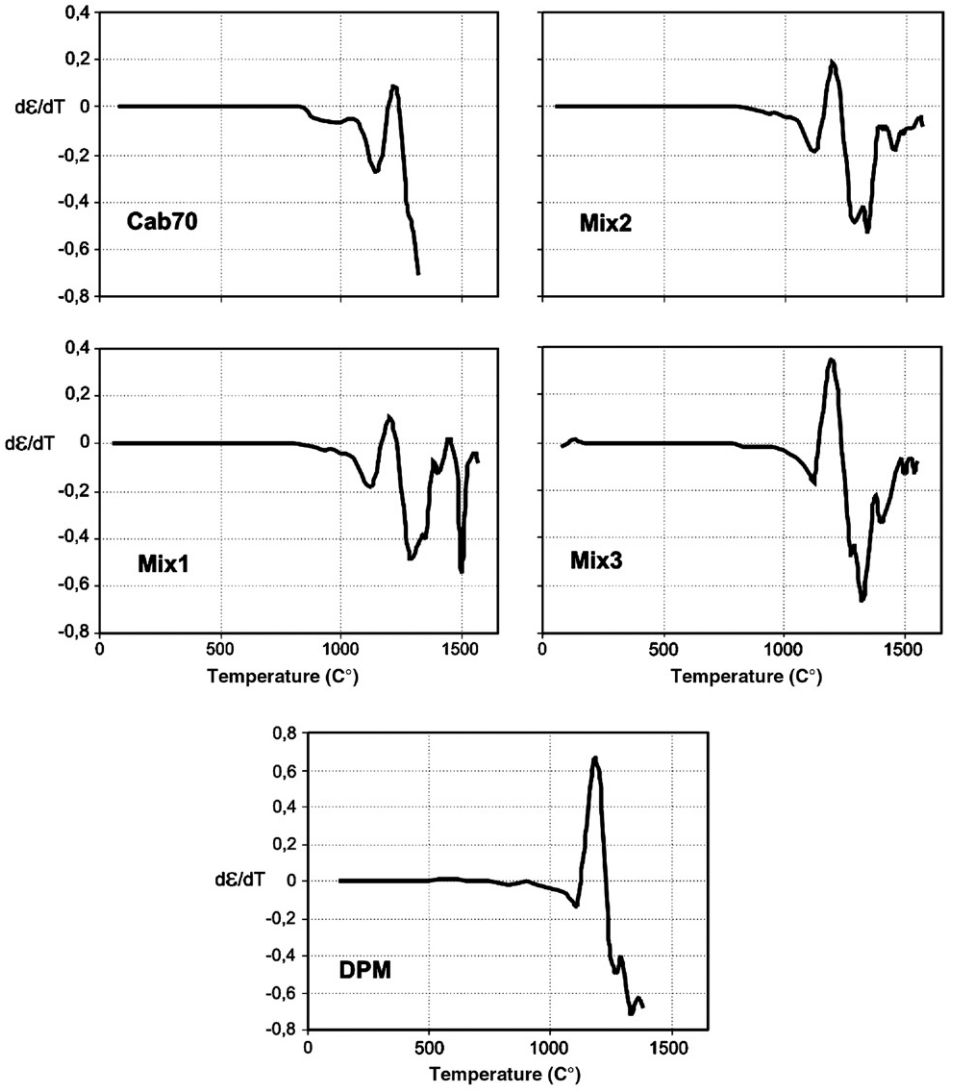

Fig. 4. Derivative of the sintering curves.

R150-15) conditions. Temperatures adopted in static conditions were 1220, 1260, 1300, 1340 and 1380 °C whereas 1260, 1300, 1340 and 1380 °C were those selected for the dynamic test. In static conditions samples were placed into the already hot muffle kiln, then removed after 5 min and quenched on air, according to the methodology described in de Gennaro et al. (2004). In dynamic conditions, rotation speed and inclination of the rotating kiln (an Al_2O_3-based refractory tube 100 cm long, inner diameter 6 cm, outer diameter 7 cm — see Fig. 1) were set to obtain firing cycles of 40–50 min cold-to-cold, with 5 min of running time in the hotter zone. Firing was always performed on granules 3–8 mm in size. To achieve this grain size from DPM and the other mixtures, 30 g of powder were pressed at 300–400 kg/cm^2. The pellets obtained (40 mm in diameter, about 14 mm in height) were hand crushed and the fragments sieved to separate the 3–8 mm fraction.

Fired products were subjected to qualitative X-ray mineralogical analyses. On samples of LEA ($Cab70_L$, $Mix1_L$, $Mix2_L$, $Mix3_L$ and DPM_L) produced in static and dynamic conditions at each tested temperature, the unit weight of the single particle was determined (UNI-7549-5, 1976). This determination was also accomplished onto unfired pellets.

Two set of LEAs were massively produced in dynamic conditions: $Cab70_L$ (LEAs from Cab70) at 1380 °C and $Mix2_L$ (LEAs from Mix2) at 1300 °C. A total volume of 5 dm^3 was gathered for each type. On these LEAs the following physical properties were measured:

- grain size analyses (UNI-7549-3, 1976);
- bulk unit weight, also called loose weight (UNI-7549-4, 1976);
- water absorption coefficient (UNI-7549-6, 1976);
- compressive strength of the particles (UNI-7549-7, 1976).

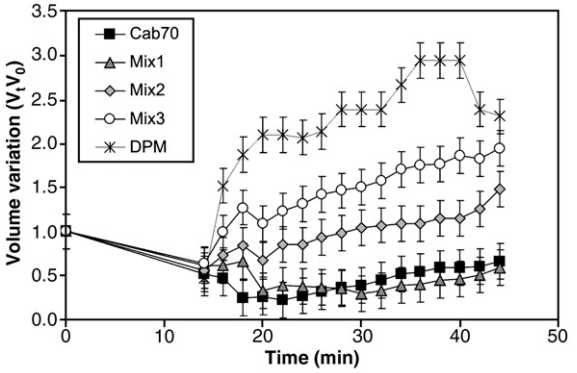

Fig. 5. Volume variation (V_t/V_0)/time at the T_{mve} indicated in Table 4 for each sample. Temperature is constant (=T_{mve}) after 14 min. V_0=-starting volume; V_t=volume at time t.

To investigate the internal structure of LEA SEM observations were carried out (Jeol, JSM 5310) at C.I.S.A.G.

3. Results

XRD analysis on Cab70 samples allows to identify phillipsite as prevailing phase along with minor amounts of chabazite and feldspar and very subordinate biotite, smectite and pyroxene (Table 2). Zeolite grade is 63±3 wt. % thus defining this material as a "zeolitite", namely a rock that can be used in those technological sectors where zeolite properties are required.

DPM is mainly constituted by glass scraped off from porcelain stoneware. Crystalline components are quartz (24±1%), along with minor quantities of calcite, mullite and zircon, and synthetic silicon carbide (moissanite-6H), that reaches about 2 wt.%.

Chemical analyses (Table 3) evidence in Cab70 a 17.04% of fluxing elements, i.e. the sum of Fe_2O_3, CaO, MgO, Na_2O and K_2O (Riley, 1969); silica and alumina are 54.52% and 15.19%, respectively. DPM is richer in silica (64.45%), whereas Al_2O_3 content is only slightly higher (16.70%) and fluxing is lower (13.51%). These values, plotted into the Riley diagram (1969), show that both Cab70 and DPM fall into the area of expanding materials (Fig. 2).

The results of fusibility tests on Cab70, DPM, Mix1, Mix2 and Mix3 are summarised in Table 4. Sintering process starts at 800–850 °C for all the samples (Fig. 3), and finishes between 1140–1210 °C (DPM and Cab70, respectively). T_r ranges between 1240 °C (Cab70) and 1180 °C (DPM). T_{me} ranges between 1255 °C (Cab70) and 1220 °C (DPM). In Mix_{1-3} both parameters decrease as in DPM increase. It should be noted that the continuous temperature increase (10 °C/min) partially hides the real potential of expansion, as samples do not have enough time to complete the bloating before melting begins. In Fig. 3 Mix3 and DPM seem the only samples able to exceed the initial volume. The T_{mve} values obtained from the derivative of the sintering curve (Fig. 4) are reported in Table 4. DPM shows the lowest T_{mve} (1184 °C), followed by Mix2 and Mix3 (1200 °C), whereas Mix1 displays a slightly higher value (1208 °C). Cab70 shows the highest T_{mve} (1234 °C). The diagrams in Fig. 4 also indicate the fastest bloating kinetic for DPM, followed by Mix3 and Mix2, whereas Mix1 and Cab70 show slower, and similar, kinetics.

Fig. 5 reports volume variations (V_t/V_0) as a function of time at the T_{mve} previously determined. All samples show a volume contraction after the 14 min required to reach their T_{mve}. Then, Mix1, Mix2, Mix3 and DPM start to bloat, whereas Cab70 still suffers a volume reduction for other 4 min. Subsequently, Cab70 is almost steady for 6 min, then starts a weak expansion, without recovering the initial volume in the tested time. Samples Mix1, Mix2 and Mix3 after 4 min of bloating (with different rates) show a sudden contraction, stronger in Mix1. Afterwards, Mix2 and Mix3 expand once again displaying subparallel trends, whereas Mix1 evidences an irregular trend, on the whole faintly increasing. Anyhow, during the last 14 min of the test, Mix1 shows a bloating lower than Cab70. DPM shows the strongest one. This sample evidences an irregular trend, reaching the highest volume after 36 min in three "steps", then it starts to contract. Samples volume variations after 34 and 44 min are reported in Table 5. It can be noted that Mix2, Mix3 and DPM achieve 1.09, 1.70 and 2.70 of their initial volume after 20 min, and final bloating attains 1.48, 1.94 and 2.30, respectively.

Table 6 reports the densities of unfired pellets and LEAs produced at different temperatures both in dynamic and static conditions. These results are plotted in Fig. 6. It can be observed that to get LEAs with the same density the rotating kiln requires temperatures generally 60–80 °C higher than the muffle kiln (Fig. 6). This difference in temperature concerns all the tests carried out in static conditions; for example, the beginning of samples contraction, after that the lowest densities are achieved, always occur at higher temperatures, except for $Cab70_L$ (the subscript L stands for LEA products) (Fig. 6 — right);

Table 5
Volume variations (normalized to the initial volume) after 34 and 44 min

Sample	Cab70	Mix1	Mix2	Mix3	DPM
T_{mve} (°C)	1234	1208	1200	1200	1183
ΔV after 34′	0.52	0.39	1.09	1.70	2.70
ΔV after 44′	0.66	0.59	1.48	1.94	2.30

Table 6
Single grain densities (g/cm^3) of LEA produced at different temperatures in dynamic and static conditions

Sample	Unfired density	Firing conditions	Firing temperature (°C)					
			1220	1260	1300	1340	1380	
Cab70	1.25	Dynamic	–	1.85	1.41	1.10	1.01	Fired density
		Static	1.30	1.10	1.05	0.95	0.90	
Mix1	1.10	Dynamic	–	1.64	1.41	0.93	0.88	
		Static	1.22	0.82	0.82	0.88	0.92	
Mix2	1.16	Dynamic	–	0.98	0.81	0.66	0.64	
		Static	0.76	0.74	0.62	0.57	0.62	
Mix3	1.18	Dynamic	–	0.92	0.68	0.53	0.54	
		Static	0.69	0.54	0.61	0.70	0.57	
DPM	1.18	Dynamic	–	0.86	0.58	0.51	0.46	
		Static	0.60	0.57	0.54	0.59	0.53	

Densities of unfired materials are also reported.

when dynamic conditions are considered, a faint increase in bulk density is observed only for $Mix3_L$ (Fig. 6 — left). $Cab70_L$ never drops below 0.90 g/cm^3, even at the highest temperature. $Mix1_L$ attains 0.82 g/cm^3 at 1260 °C when prepared in static conditions, 0.88 g/cm^3 at 1380 °C in dynamic ones. The lowest density of $Mix2_L$ ranges from 0.57 (1340 °C — static) to 0.64 g/cm^3 (1380 °C — dynamic). $Mix3_L$ attains substantially the same lowest density (0.53–0.54 g/cm^3) at 1340 °C by using the rotating kiln, but as low as 1260 °C with the muffle. When fired in static conditions, DPM_L densities fluctuate between 0.60–0.53 g/cm^3, whereas a decreasing trend (from 0.86 g/cm^3 at 1260 °C to 0.46 g/cm^3 at 1380 °C) is observed for DPM_L prepared in dynamic conditions. Finally, it can be noted that $Mix2_L$, $Mix3_L$ and DPM_L always show densities lower than the corresponding unfired materials (Table 6).

On the whole, all the materials fired in dynamic conditions show a clear inverse relationship between density and temperature, as well as between DPM amount in the material and density (Fig. 6 — left). At the same temperatures these links are less evident in static conditions, and can be observed for $Cab70_L$, $Mix1_L$ and $Mix2_L$ only (Fig. 6 — right).

Mineralogical analyses reveal the presence of glass in all fired products. Furthermore, glass content increases with temperature. Besides feldspar and pyroxene, already found in unfired material, all LEAs contain leucite as result of transformation processes involving K-rich chabazite and phillipsite. Quartz, mullite and zircon are relict phases present in LEAs produced with DPM.

Table 7 reports a set of technical features determined onto the aggregates $Cab70_L$ and $Mix2_L$ massively produced. The results are compared to some expanded clays, similar in grain size range, commercialised in Italy (Leca® products, manufactured by Laterite S.p.A., Milan, Italy; data extrapolated at www.leca.itwebsite). $Mix2_L$ show higher technical performances than $Cab70_L$ ones not only in terms of density, as already seen, but also in

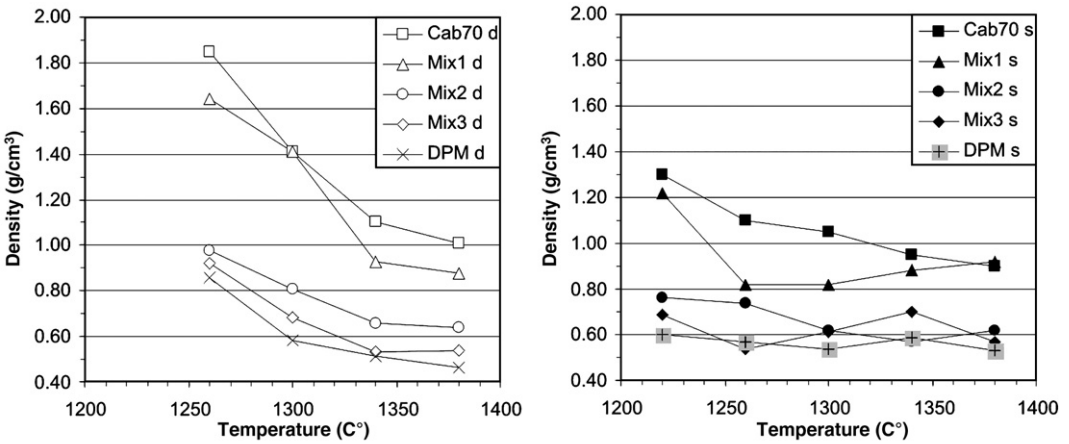

Fig. 6. Effect of DPM addition on the density of LEA produced at different temperatures in: dynamic (left) and static (right) conditions. DPM content is (wt.%): Cab70 = 0%; Mix1 = 15%; Mix2 = 30%; Mix3 = 50%; DPM = 100%.

Table 7
Technical features of Cab70 and Mix2 LEA compared to some expanded clays commercialised in Italy (Leca® — Light expanded clay aggregate, manufactured in Italy by Laterite S.p.A., Milan)

Technical feature		$Cab70_L$	$Mix2_L$	Leca	Lecapiù	Leca Strutturale
Grain size range	mm	3–10	3–10	3–8	3–8	3–15
Loose weight	kg/m^3	565	460	380	360	770
Density (single grain)	g/cm^3	1.01	0.81	0.65	0.65	1.3
Water absorption coefficient after 30 min	%	3.3	0.7	7	<1	>4
Water absorption coefficient after 24 h	%	5.7	1.4	11	–	>7
Compressive strength (single grain)	MPa	0.6	2.9	1.5	1.5	4.5
Compressive strength/density	kJ/kg	0.59	3.58	2.31	2.31	3.46

terms of loose weight (460 vs. 565 kg/m^3), water absorption coefficients (0.7 vs. 3.3% after 30 min; 1.4 vs. 5.5% after 24 h) and compressive strength (2.9 vs. 0.6 MPa). Fig. 7 reports the grain size distribution of $Cab70_L$ and $Mix2_L$. Although all aggregates were prepared using unfired material of the same dimension (3–8 mm), final grain size distributions are different. $Mix2_L$ show an almost symmetric distribution with 45 wt.% of the samples within the 5–7 mm range. Unlike $Mix2_L$, $Cab70_L$ display an asymmetric distribution, shifted toward a larger size: 55 wt.% of the samples belong to the 7–10 mm class, in spite of a bloating lower than $Mix2_L$. Macroscopic (Fig. 8) and microscopic (Fig. 9) images of these LEAs show the different degree of vesiculation of the products. $Mix2_L$ evidences bubbles more regular in shape and dimensions and more homogeneously distributed than $Cab70_L$. Furthermore, the thickness of the walls between larger pores is higher in $Mix2_L$ than in $Cab70_L$, and small bubbles inside the wall are more abundant in $Mix2_L$ (Fig. 9).

4. Discussion

It is well known that, to get a thermally expandable material, a suitable chemical composition influencing the "softening" at high temperature is required as well as the presence of substances able to develop gas (such as water, carbon dioxide, oxygen, etc.) upon heating (Riley, 1969). According to Riley's diagram, the chemical composition of the zeolitized facies of the Campanian Ignimbrite perfectly overlaps the area corresponding to expanding materials (Fig. 2). Furthermore, this facies shows a L.o.I. higher than 12 wt.% (Table 3), so that gas, namely water vapor, is released upon heating as a consequence of dehydration and dehydroxylation processes. In spite of this feature, the fusibility test evidences a reduced expansion (Figs. 3 and 4), and when kept for 30 min at T_{mve} it never exceeds the initial dimension, and even exhibits a contraction (Fig. 5). However, a limited bloating has been observed both in static (for $T \geq 1260$ °C) and in dynamic (for $T \geq 1340$ °C) firing experiments (Fig. 6), but densities lower than 1 g/cm^3 were reached only in static conditions at temperatures

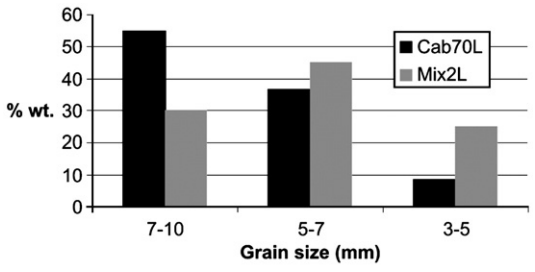

Fig. 7. Grain size distributions of $Cab70_L$ and $Mix2_L$ massively produced.

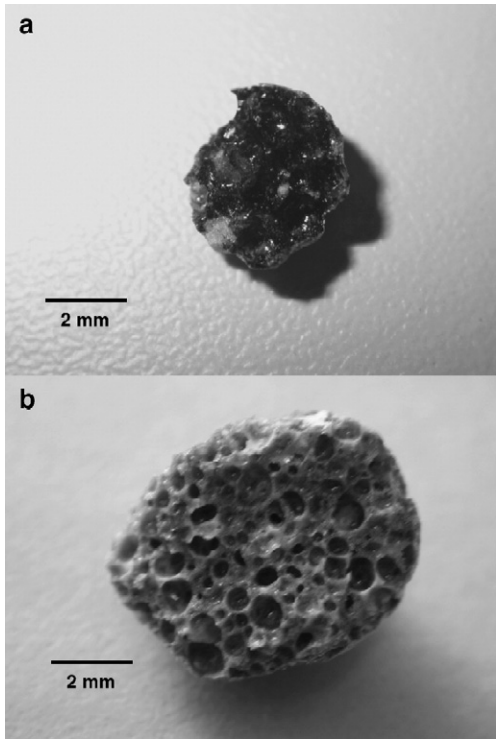

Fig. 8. LEA produced in dynamic conditions: a) $Cab70_L$ (at 1380 °C) and b) $Mix2_L$ (at 1300 °C).

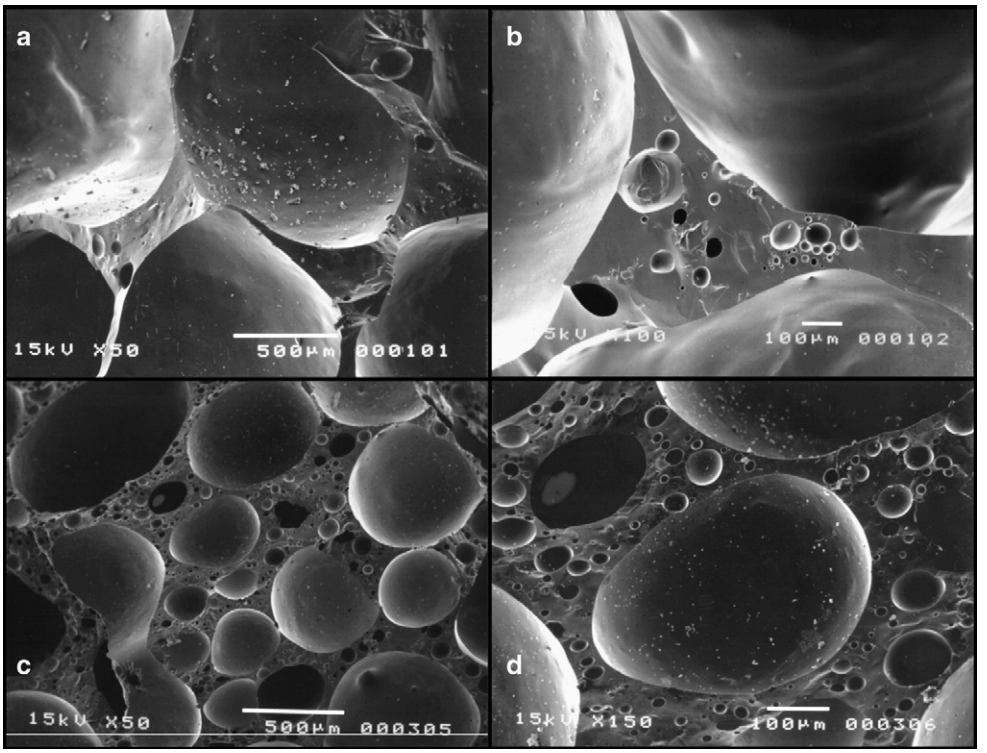

Fig. 9. SEM images of LEA produced in dynamic conditions. $Cab70_L$ (a; b) and $Mix2_L$ (c; d).

≥1340 °C (Table 6). Such temperatures are higher than those usually employed to get industrial LEAs (ANPAE, 2003). Furthermore, LEAs produced using clays show a density between 0.5–0.7 g/cm^3. To achieve the same values using a zeolitized tuff the rock should have a L.o.I. higher than 10%, a SiO_2/fluxing ratio between 4 and 7.5, and a SiO_2/Al_2O_3 ratio in the 4–5.6 range (de Gennaro et al., 2004). Cab70 characterized by a SiO_2/fluxing ratio=3.2 and a SiO_2/Al_2O_3 ratio=3.6 (calculated from data of Table 3), during firing process attains a low viscosity that allows only a partial entrapment of the gas developed (de Gennaro et al., 2004). However, it cannot be excluded that bloating, at least partially, could be related to the occurrence of water evolved as a consequence of dehydroxilation process. Kazantseva and Paukshtis (2000) in particular underline that, the amount of zeolite-bearing tuff being equal, the gaseous phases produced during thermally induced foaming of zeolitic tuffs depends on the content of divalent cations (Ca and others) in the tuff itself. This peculiar chemical composition determines the formation of structural hydroxyl groups. Upon heating up to 1200 °C zeolites rich in divalent cations only show a partial dehydration; residue water molecules undergo dissociation by hydrolysis; dehydroxylation and H_2O-molecules formation follow. At temperature >900°–1000 °C (sintering temperature) the water vapor formed is enclosed in micropores and escapes at 1200 °C (melting temperature) thus determining the bloating of the tuff.

The fusibility tests have evidenced a marked bloating of DPM. In particular, after 22 min at its T_{mve} DPM almost triplicates the initial volume (Fig. 5), and LEAs obtained at 1380 °C in dynamic conditions show a density of 0.46 g/

Table 8
Effect of DPM addition to Cab70 (see text for explanations)

Δd (g/cm^3) — density referred to $Cab70_L$						
Dynamic conditions			Temperature (°C)	Static conditions		
$Mix1_L$	$Mix2_L$	$Mix3_L$		$Mix1_L$	$Mix2_L$	$Mix3_L$
–	–	–	1220	0.08	0.54	0.61
0.21	0.87	0.93	1260	0.28	0.36	0.56
0.00	0.60	0.73	1300	0.23	0.43	0.44
0.17	0.44	0.57	1340	0.07	0.38	0.25
0.13	0.37	0.47	1380	−0.02	0.28	0.33
Benefit factor (g/cm^3) — Δd/DPM fraction						
–	–	–	1220	0.53	1.80	1.22
1.40	2.90	1.86	1260	1.87	1.20	1.12
0.00	2.00	1.46	1300	1.53	1.43	0.88
1.13	1.47	1.14	1340	0.47	1.27	0.50
0.87	1.23	0.94	1380	−0.13	0.93	0.66
0.15	0.30	0.50	DPM fraction	0.15	0.30	0.50

cm^3. It should be noted that the SiO_2/fluxing and SiO_2/Al_2O_3 ratios for DPM are 4.8 and 3.9, respectively (calculated from data in Table 3). These values are close to those required to obtain a suitable viscosity during firing process (de Gennaro et al., 2004). On the other hand, DPM displays a L.o.I. noticeably lower than Cab70 (4.68 vs. 12.53 wt.%), as it is essentially related to carbon dioxide resulting by SiC decomposition and not to water evolution as in Cab70. This depends on the fact that water release in Cab70 occurs well before the material reaches a pyroplastic state, whereas SiC decomposition in DPM — requiring a higher temperature than water evolution — occurs when the material is in, or close to, the pyroplastic state. All these factors determine a more effective action of gas developed in DPM than in Cab70 so that, at a given temperature, the bloating increases with SiC content (see Table 6 and Fig. 6). The derivatives of the sintering curves demonstrate that the addition of DPM to Cab70 also determines a progressive lowering of the temperatures at which bloating kinetic reaches the maximum (Fig. 4; Table 4). It can be summarized that the addiction of DPM to Cab70 determines a reduction of the temperatures required for bloating and a bloating enhancement, as confirmed by data of Table 6. Anyhow, the relationship between DPM content and density decrease (Δd) is not linear, as it can be noted in Table 8 (top) where $Mix1_L$, $Mix2_L$ and $Mix3_L$ densities are compared to $Cab70_L$ produced at the same temperature. This behavior can be observed both in static and in dynamic conditions. For a given mixture Δd generally decreases with temperature. This depends on the fact that Cab70 — chosen as reference — shows the highest densities, but also evidences the strongest bloating improvement in the 1220–1380 °C range (Table 6): from 1.30 to 0.90 g/cm^3 (static); from 1.85 to 1.01 g/cm^3 (dynamic). Generally, the trends here described are more regular for LEAs produced with the rotary kiln, whereas among the three mixtures, Mix1 shows the less regular trend (Table 8 — top).

It is useful to define, for a given temperature, which is the lowest DPM content able to determine the strongest density reduction in the three fired mixtures. Table 8 (bottom) introduces the "Benefit factor", that is the ratio between Δd and DPM content. It can be noted that in dynamic conditions Mix2 always shows the highest Benefit factors, whereas in static ones this is true three times out of five. Data demonstrate that the strongest gain in expansion is obtainable by admixing 30 wt.% of DPM to Cab70, and firing in dynamic conditions from 1260 °C (B.f.=2.90 g/cm^3; final LEA density=0.98 g/cm^3) to 1300 °C (B.f.=2.00 g/cm^3; final LEA density=0.81 g/cm^3).

There are differences between the firing temperatures required to obtain the same expansion in static or in dynamic conditions. These differences should be related to the different thermal insulation of the two systems during firing. The rotating kiln operates with the inclined tube always opened at the extremities (Fig. 1). This determines a light, but continue, ingoing of cold air and outgoing of hot air. On the contrary, the muffle kiln — during the 5 min of firing — is a system thermally closed. Hence, when the two systems are settled at the same firing temperature, the efficiency in heat transmission to the samples cannot be the same. This explains the "delay" effect observed at the rotating kiln with respect to the muffle. On the other hand the rotating kiln produces LEAs more spherical in shape and, much more, it more closely simulates LEA industrial production process (Silva and Peres, 2006).

The technical features determined onto the aggregates massively produced (Table 7) show that $Mix2_L$ displays a very low water absorption coefficient, comparable to "Lecapiù", a commercial product specifically employed to create barriers against humidity. Moreover, $Mix2_L$ exhibits a compressive strength/density ratio even higher than "Leca Strutturale" (3.58 vs. 3.46 kJ/kg), that is a high-resistant LEA. On the contrary, technical parameters of $Cab70_L$ are the worst among the considered materials. In particular, the compressive strength/density ratio attains a very low value (0.59 kJ/kg). As far as LEAs are concerned, this parameter can represent a measure of the compromise obtained between the needs of high compressive resistance and low density. The better performances of $Mix2_L$ with respect to $Cab70_L$ can be explained by the different structures observed (Figs. 8 and 9). Few large pores, irregular in shape, give to $Cab70_L$ a less expanded and less resistant structure than $Mix2_L$. The scarce homogeneity of pore distribution in $Cab70_L$ can be related to the natural heterogeneity of the material, also in terms of spatial distribution of mineralogical phases. It should be remarked that $Cab70_L$ were prepared employing a 3–8 mm rock granulate, whereas the starting material used for $Mix2_L$ was a fine powder (<200 μm) from which homogenous pellets were derived (see Materials and methods paragraph). This difference between the unfired pellets also explains the different grain size distributions of $Cab70_L$ and $Mix2_L$ (Fig. 7). In spite of a lower bloating, $Cab70_L$ shows a prevalence of larger grains than $Mix2_L$. This is why Cab70 unfired pellets have the consistence of the natural rock, whereas Mix2 pellets, obtained by pressing powders, tend easily to disaggregate during firing operations.

5. Conclusions

The above reported results suggest that the zeolitized facies of Campanian Ignimbrite can be a promising raw

material for the production of LEAs with a density of about 1 g/cm^3. Although from a technological point of view these LEAs do not evidence high performances — particularly in terms of compressive strength — they could be employed when only insulating properties are required (for example, in the manufacture of lightweight concrete). It is noteworthy that the production of these LEAs needs only the granulation of a low-cost raw material before firing. On the other hand, firing temperatures are slightly higher than those generally used to get LEAs.

LEAs with much better technological features can be achieved by admixing 30 wt.% of DPM to Cab70. This mixture requires firing temperatures generally close to those used in the industrial production. LEAs with a density from 0.98 to 0.81 g/cm^3 can be produced at 1260–1300 °C, respectively. The technical parameters of these LEAs are analogous to — and sometimes even better than — the expanded clays commercialised in Italy. The availability of DPM in Italy is quite high, taking into account that, even by considering only the Sassuolo–Scandiano district, mud production attained 46,000 t/year already in 1999. This quantity, with a Cab70/DPM weight ratio of 70/30, would be enough to produce from 156,000 to 189,000 m^3 of LEAs, depending on the firing temperatures selected. These volumes represent the 15.6–18.9% of the estimated LEA Italian production. In addition, it should be underlined that DPM, the dry mud coming from the polishing process of porcelain stoneware tiles, is a waste currently not recycled at all, thus representing a problem for the environment as well as for the ceramic industry. Given the continuous growth of porcelain stoneware production in Italy during the last years, it can be hypothesized that there is an increase of the related waste too. Consequently, a plant employing this industrial residue would guarantee supplies of raw material.

The results obtained open new perspectives on the use of the Campanian Ignimbrite and on the recycling of the mud employed in the polishing of porcelain stoneware tiles. Some aspects are worth of further studies in view of an eventual industrial development. For example, the pellet forming process necessary to prepare the granules to be expanded needs improvements. Furthermore, a reduction of firing temperatures should also be investigated, and new bloating agents could be tested.

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