

# Use of zeolite-rich rocks and waste materials for the production of structural lightweight concretes

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## Abstract

This paper aims at testing the use of mixtures constituted by natural zeolitized products and SiC-bearing industrial wastes (sludge deriving from polishing of porcelain stoneware tiles, hereafter DPM) for the production of lightweight expanded aggregates as constituents of structural and/or thermo-insulating lightweight concretes. Two commercial products have been used as zeolite natural source: Cab70 (Yellow facies of Campanian Ignimbrite) and IZclino (Turkish clinoptilolite-rich epicalastite). Different amounts of a calcareous material (Pozzano limestones — hereafter CP) from the Sorrento peninsula (Naples — Italy) were also added to a Cab70–DPM mixture. All raw materials were characterized by means of mineralogical (XRPD) and chemical (XRF) analyses. All the products and mixtures were tested from a technological point of view by means of fusibility and firing tests in order to evaluate the expanding properties. It was evidenced that the expansion of the mixture was deeply depending on the occurrence of SiC in the industrial waste. The addition of CP (10 wt.%) to the mixtures accounts for an even increased expansion, though this is accompanied by a worsening of the mechanical features of the material.

These results along with literature data allowed to select 3 mixtures (70% Cab70–30% DPM, 70% IZclino–30% DPM, 60% Cab70–30% DPM–10% CP) and each of them was used for the preparation of 5 l of lightweight aggregates afterward employed for the manufacture of lightweight concretes. It was remarked that natural zeolitized materials mixed with DPM (30 wt.%) can provide lightweight aggregates with densities ranging between 0.8 and 1.0 g/cm<sup>3</sup> suitable for the preparation of structural lightweight concretes. The addition to the mixture of CP (10 wt.%) produces less dense aggregates (0.6–0.7 g/cm<sup>3</sup>) potentially useful for the manufacture of thermo insulating lightweight concretes.

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## 1. Introduction

Lightweight concretes are cementitious conglomerates with a bulk density (ranging between 300 and 2000 kg/m<sup>3</sup>) sensibly lower than that of an ordinary concrete (usually between 2200 and 2600 kg/m<sup>3</sup>) (Collepardi, 2002). On the

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basis of their dry bulk density and compressive mechanical strength, both evaluated after an aging period of 28 days, they can be classified as follows:

- *Thermo insulating lightweight concretes*: bulk density: 300–800 kg/m<sup>3</sup>; compressive mechanical strength: 0.5–7 MPa. Preferentially used as filling material or as insulating coatings (Collepari, 2002).
- *Low strength lightweight concretes*: bulk density: 800–1400 kg/m<sup>3</sup>; compressive mechanical strength: 7–18 MPa. They are prevalently used in structures which do not require particular performances from a static point of view. At the same time, they guarantee an acceptable level of thermal comfort (Collepari, 2002).
- *Structural lightweight concretes* bulk density: 1400–2000 kg/m<sup>3</sup>; compressive mechanical strength: >20 MPa (Suppl. Ord. G.U.R.I., 1996a,b). These concretes, usually manufactured with artificial inert, are used for the production of low density reinforced structures (Collepari, 2002).

The reduced bulk density of a lightweight concrete is due to the addition of a void system within the cementitious conglomerate (Short and Kinniburgh, 1978). Three different ways can be followed to achieve this result (Collepari, 2002):

- by replacing the usual inert matter with natural or artificial lightweight inert characterized by high porosity;
- by using an inert matter constituted by small polystyrene balls;
- by adding to the mixture a pre-formed foam or substances able to develop gases in an alkaline environment. This procedure determines the formation of a 1 mm bubble system.

Lightweight inert used for the manufacture of lightweight concretes is characterized by a highly porous microstructure and, consequently, by a loose weight (<1200 kg/m<sup>3</sup>) lower than that of inert matter used in ordinary concretes (1500–1700 kg/m<sup>3</sup>) (Collepari, 2002). Lightweight inert matter can be natural (pumice, diatomites, etc.) or artificial (expanded aggregates), the latter obtained by natural or artificial materials after a processing cycle able to create a cellular or highly porous structure. The natural raw materials (usually clay or shale) contain substances able to develop gases during the heating stage at temperatures close to those at which the material begins to soften. In these conditions a very viscous liquid phase is formed and it is able to entrap the gas developed and thus allowing the aggregate expansion (Riley, 1969; Collepari, 2002; de Gennaro et al., 2007).

This process is carried out in large rotating furnaces (diameter around 4.5 m; length around 70 m) at temperatures that can even reach 1300 °C (ANPAE, 2003). After cooling the product occurs as spherical aggregates with an inner cellular microstructure and a glassy surface providing the inert with a good mechanical strength and a low water absorption (Collepari, 2002). Based on the European Union regulations (UNI EN 13055-1, 2002) lightweight aggregates must have a unit weight of particle lower than 2000 kg/m<sup>3</sup> and loose weight lower than 1200 kg/m<sup>3</sup>.

The use of zeolitized material for the production of lightweight aggregates and artifacts is well known since many years (Mumpton, 1978; Torii, 1978; Gayoso Blanco et al., 1991; Kazantseva et al., 1996 and 1997) including those occurring on the Italian territory (Sistu, 1990; Sistu and Atzeni, 1993; de Gennaro et al., 2001, 2004, 2005 and 2007). In particular, it was observed that the addition of sludge deriving from polishing of porcelain stoneware tiles (30 wt.%) to Campanian Ignimbrite (Cab70) allowed the production of lightweight aggregates with technical features definitely better than those of commercial expanded clays (de Gennaro et al., 2007). The high expanding ability of this sludge is due to the presence of silicon carbide (polishing abrasive agent) that produces large amounts of gas by dissociation at temperatures close to those at which the waste starts softening (de Gennaro et al., 2007). These temperatures also correspond to the softening temperatures of the considered zeolite-rich materials used in the mixtures.

On the basis of the above considerations, the aims of the research are: 1) testing the use of a clinoptilolite-rich epiclastite from Turkey (IZclino), mixed with DPM (Dry Polishing Mud), as a raw material for the production of lightweight aggregates; 2) assessing the addition of calcium carbonate contained in a limestone (CP) to a mixture of Cab70 and DPM as further melting agent; 3) scaling up the best mixtures to a mass production of three different types of lightweight aggregates and lightweight concretes.

## 2. Materials and methods

Raw materials used for the present investigation are: two commercial zeolitites (Cab70 and IZclino) distributed by the “Italiana Zeoliti s.r.l.” company from Pigneto (Modena — Italy); a sludge (DPM) from polishing of porcelain stoneware tiles from the ceramic district of Sassuolo (Italy); a limestone (CP) from Pozzano (Sorrento peninsula, Naples — Italy).

Cab70 was obtained by grinding and sieving samples of Campanian Ignimbrite collected in a quarry in Comiziano (Naples). Campanian Ignimbrite represents one of the main

pyroclastic products of Southern Italy (Cappelletti et al., 2003) emplaced about 39 ky b.p. (De Vivo et al., 2001). The yellow facies, representing one out of four stratigraphic Units, underwent deep zeolitization processes that brought about the formation of phillipsite and chabazite, sometimes occurring in amounts higher than 60 wt.% (Cappelletti et al., 2003).

IZclino is a Turkish clinoptilolite-bearing epiclastite outcropping within the Kirka basin, on the South side of the town of Eskisehir (Sengör 1980; Sengör and Yilmaz 1981; Sengör et al., 1985). The lacustrine facies of the Kirka basin is characterized by coarse to fine grain size epiclastites altered to zeolites (clinoptilolite) and other diagenetic minerals (Yalçın 1989; Yalçın and Baysal, 1991).

The limestone used for the experiments (CP) was collected in the north-west dipping well stratified Cretaceous succession widely outcropping in the Pozzano area (Naples) (Calcaterra and Santo, 2004).

The industrial waste (DPM), coming from the treatment of waters used for polishing of porcelain stoneware tiles, is considered “non-dangerous” by the Italian and European laws (Dlgs 5-2-97 n.°22, 1997). This waste contains mostly powder of porcelain stonewares plus a low amount (1–2 wt.%) of the abrasive: silicon carbide (de Gennaro et al., 2007). The annual production of this waste is some 50,000 tons (ANPA, 2002). No specific use of this material was proposed so far and, since at least a decade, it is simply disposed in dumping areas.

The mineralogical characterization was carried out on powdered samples of the raw materials and of fired products by XRD (CuK $\alpha$  radiation, 40 kV, 30 mA) using an X’Pert instrument (PANalytical). Quantitative mineralogical analysis was carried out using the “Reference Intensity Ratio” (RIR) technique (Bish and Chipera, 1988).

Chemical analyses were performed in XRF using an Axios apparatus (PANalytical) at C.I.S.A.G. (Centro Interdipartimentale di Servizio per Analisi Geomineralogiche, Università di Napoli). Data were corrected by drifting and background effects, and reduced using the method proposed by Melluso et al. (2005). Analytical accuracy is around  $\pm 1\%$  for SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, K<sub>2</sub>O and MnO;  $\pm 4\%$  for MgO, Na<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>. Loss on ignition was measured after sample firing for two hours at 1200 °C.

Preliminary technological characterizations were carried out by means of fusibility tests and firing tests on the IZclino sample and the following mixtures:

Mix 1: 65% Cab70, 30% DPM, 5% CP  
 Mix 2: 60% Cab70, 30% DPM, 10% CP  
 Mix 3: 55% Cab70, 30% DPM, 15% CP  
 Mix 4: 50% Cab70, 30% DPM, 20% CP  
 Mix 5: 90% IZclino, 10% DPM  
 Mix 6: 70% IZclino, 30% DPM  
 Mix 7: 50% IZclino, 50% DPM

In order to better understand the role of CP during the firing stage, tests were also carried out on Cab70/CP mixtures without DPM at 1300 °C.

Fusibility tests were carried out with a heating microscope (Expert System Solutions, Misura 2, heating rate 10 °C/min) on cylindrical specimens (3 mm height, 1 mm diameter) until melting was achieved. The shape variation of the specimen was interpreted in order to draw the sintering curve and to get the characteristic temperatures (Dondi et al., 2001).

Firing tests were carried out on 3–10 mm pellets with bulk density of about 1.20 g/cm<sup>3</sup>, obtained by pressing (300–400 kg/cm<sup>2</sup>) the IZclino powders and the above described mixtures. Pellets were fired in a rotating kiln (Nannetti mod TO-R150-15) following the procedure described by de Gennaro et al. (2007). IZclino sample and IZclino-DPM mixtures were fired at 1300, 1340 and 1380 °C, whereas Cab70–DPM–CP mixtures were treated at 1260, 1280 and 1300 °C. Unit weight of particle of fired materials was measured according to the Archimede principle (de Gennaro et al., 2004):

$$d = (W_3 * \gamma_w) / (W_1 - W_2 + W_3)$$

where  $W_3$  is the dry weight of the fired pellet,  $\gamma_w$  is the density of distilled water (assumed as 1 g/cm<sup>3</sup>),  $W_1$  is the weight of a 10 ml water filled beaker and  $W_2$  is the weight of the same beaker with water and pellet.

Finally, Mixes 2 and 6 and another one (Mix 0) obtained mixing Cab70 (70%) and DPM (30%), selected on the basis of previous data (de Gennaro et al., 2007), were used to produce 5 liters of lightweight aggregates for each sample. The following physico-mechanical tests were carried out on these aggregates: grain size distribution, loose weight, strength of particles (UNI EN 13055-1, 2002), water absorption (UNI EN 1097-6, 2002). Some tests on conventional concrete (UNI 11013, 2002) were also carried out at CEMENTIR (Cementerie del Tirreno S.p.A., Spoleto — Perugia) laboratories (CRQ — Centro Ricerche e Qualità).

Table 1 reports the components of the mixtures used to produce concretes. In order to obtain more cohesive mixtures the lightweight aggregate was partly replaced by a higher amount of sand (about 100 l corresponding to more than 300 kg) with respect to what suggested by the UNI 11013 (2002).

Mixture components are hereafter described:

- 1) lightweight aggregate (Mix2, Mix6, Mix 0)
- 2) ordinary sand, silica-rich sand with a grain size distribution corresponding to that of those sands generally used to produce ordinary mortars according to UNI EN 196-1 (2005).

Table 1  
Components of mixture for concrete

Component	Amount
Cement kg/m <sup>3</sup>	350
Sand kg/m <sup>3</sup>	833
A/C	0.46
Sky 528-Mac Degussa Additive l/m <sup>3</sup>	4.55
Lightweight aggregate l/m <sup>3</sup>	400
Encapsulated air l/m <sup>3</sup>	30

Table 2  
Quantitative mineralogical composition of zeolitized materials

wt. %	Cab70		IZclino	
	Mean	Error	Mean	Error
Phillipsite	40	2	–	–
Chabazite	5	1	–	–
Clinoptilolite	–	–	59	3
Feldspar	24	3	16	2
Smectite	4	1	4	1
Quartz	5	1	9	1
Opal	–	–	5	1
Calcite	4	1	–	–
Analcime	6	1	–	–
Biotite	tr.		tr.	
Total	88	10	93	8

- 3) Cement, CEM I-42 type, 5R according to [UNI EN 197-1 \(2006\)](#), characterized by a compressive strength not higher than 55 MPa after 28 days in an ordinary mortar.
- 4) Fluidizing additive, Glenium SKY 528 type — Mac Degussa.
- 5) Water for mixture, potable, conditioned to the laboratory temperature.

Mixtures were always set at 20 °C and RH>65%. The flow table test was carried out as soon as the mixtures were prepared, following the procedure described in [UNI EN 12350-5 \(2001\)](#). After that, mixtures were poured out in moulds to manufacture three cubes (10 × 10 × 10 cm) for each. The moulds with mixtures were carefully stored for three days at room temperature (20 °C). The cubes were then removed from the moulds and immersed in water at 20 °C to complete the aging period (28 days). At the end of this period they were air dried for two hours and bulk density ([UNI 7548-2, 1992](#)) and compressive strength ([UNI EN 196-1, 2005](#)) measured. Both lightweight aggregates and concretes were carefully observed on scanning electron microscope (Jeol 5310-SemAfore) at C.I.S.A.G.

### 3. Results

[Table 2](#) reports the mineralogical compositions of the two natural materials. Cab70 shows phillipsite as the main constituent along with chabazite and feldspar. Minor amounts of biotite and smectite were also recorded. The occurrence of few units percent of calcite and quartz should be likely due to a sort of “pollution” related to the working operations, since these phases are not compatible with the paragenesis of Campanian Ignimbrite. Clinoptilolite is the most abundant phase in IZclino always occurring along with feldspar, quartz, opal-CT, smectite and traces of biotite. The high zeolite content (>50 wt.%) in both samples defines these materials as zeolitites that is, rocks that can be used in technological sectors which exploit zeolite properties.

DPM is mainly constituted by the glassy fraction of porcelain stonewares whereas the crystalline portion is represented by quartz (24%), deriving by the ceramic product and the polishing abrasive agent, and subordinated by mullite and minor amount of zircon, moissanite 6H (SiC ~ 2%) and calcite (<1%).

Calcite and subordinate dolomite (99 wt.%) are the main constituents of Pozzano limestones. The insoluble residue is characterized by mica, feldspar, kaolinite, pyroxene, iron and titanium oxides.

Chemical compositions of the above described materials are reported in [Table 3](#). IZclino and DPM show the highest (>5) SiO<sub>2</sub>/fluxing (Fe<sub>2</sub>O<sub>3</sub>+MgO+CaO+Na<sub>2</sub>O+K<sub>2</sub>O) whereas the same ratio for Campanian Ignimbrite (Cab70) is slightly higher than 3. Loss on Ignition (LOI) in natural samples is mainly due to zeolitic water and, for Cab70 only, also to calcite dissociation. As far as DPM is considered LOI can be attributed to the dissociation of silicon carbide (SiC) and of calcite.

Representative points of IZclino, Cab70 and DPM plotted in [Riley's diagram \(1951\)](#) fall within the area pertaining to the expandable materials ([Fig. 1](#)).

Sintering curves ([Fig. 2](#)) evaluated on Mixes 1 ÷ 7 show a volume decrease for all the samples beginning at 800–850 °C. Over the sintering temperature ( $T_s$ ), specimens start to soften ( $T_r$ ) and increase their volume until the temperature of the maximum expansion ( $T_{me}$ ) is reached. Further on, specimens shrink up to the melting temperature ( $T_f$ ). Characteristic temperatures of Mixes 1 ÷ 4 exhibit similar sintering and softening temperatures ([Table 4](#)); increasing the CP content, the melting temperature gradually decreases from 1280 °C (Mix 1) to 1215 °C (Mix 4).

Table 3  
Chemical composition of the materials

wt. %	Cab 70	IZclino	DPM	CP
SiO <sub>2</sub>	54.52	65.65	68.44	1.36
TiO <sub>2</sub>	0.45	0.23	0.55	<0.01
Al <sub>2</sub> O <sub>3</sub>	15.19	13.20	16.41	0.03
Fe <sub>2</sub> O <sub>3</sub>	4.00	2.55	0.17	0.03
MnO	0.17	0.05	0.02	<0.01
MgO	0.88	1.44	5.60	3.13
CaO	4.14	1.63	0.98	51.7
Na <sub>2</sub> O	1.04	1.35	0.81	0.04
K <sub>2</sub> O	6.98	4.30	2.21	0.01
P <sub>2</sub> O <sub>5</sub>	0.10	0.01	0.12	<0.01
LOI	12.53	9.83	4.68	43.69
Fluxing	17.04	11.27	9.78	54.91
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	3.59	4.97	4.17	–
SiO <sub>2</sub> /fluxing	3.2	5.8	7.0	–



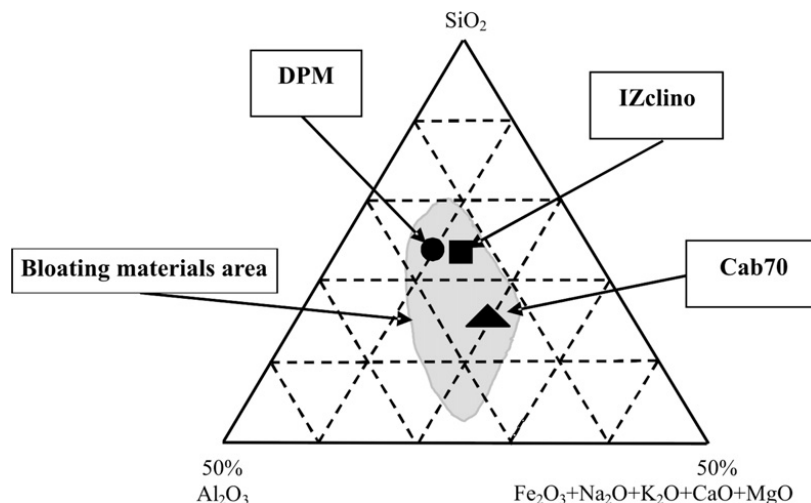


Fig. 1. Riley's diagram (1969).

IZclino and Mixes 5 ÷ 7 are characterized by higher characteristic temperatures with respect to Mixes 1 ÷ 4: softening temperatures always exceed 1200 °C, whereas melting temperatures are close to 1400 °C. The  $T_{me}$  ranges from 1335 °C in IZclino to 1280 °C in the Mix 7. All characteristic temperatures decrease when the DPM content increases (Table 4).

Table 5 reports the firing tests carried out in a rotary kiln on IZclino and mixtures compared with literature data. Previous researches (de Gennaro et al., 2007) showed that the addition of DPM (30%) to Cab70 determined a sharp decrease in unit weight of particle of fired products. The present results proved that a 10% of CP into the mixture, in place of Cab70, determines a further decrease of the unit weight of particle reaching values slightly higher than 0.60 g/cm<sup>3</sup> at 1300 °C. Contents higher than 10% of CP do not seem to improve the parameter. As far as Cab70/CP mixtures without DPM at 1300 °C, results (Table 6) evidenced that the material does not expand, giving final unit weight of particle even higher than those measured on unfired pellets.

As far as IZclino sample without any addition (Table 5) is concerned, none of the investigated temperatures allowed to provide aggregates with unit weight of particle lower than 1 g/cm<sup>3</sup>. Unlike IZclino sample, increasing amounts of DPM as well as increasing temperatures for Mixes 5 ÷ 7 favour the expansion with consequently lower unit weight of particle of the fired products. The lowest values (0.56 g/cm<sup>3</sup>) were achieved in Mix 7 (the highest DPM content) at 1380 °C (the highest temperature).

Useful expansions in IZclino-DPM mixtures were obtained at temperatures higher than those recorded for Cab70-DPM-CP mixtures, as previously tested during the fusibility tests.

Based on the above results and referenced literature, the following mixtures and firing temperatures were selected to produce 5 l of Lightweight Expanded Aggregates (LEA) to be used for the physico-mechanical characterization:

- LEA1: Mix 2, firing temperature 1300 °C;
- LEA2: Mix 0, firing temperature 1300 °C;
- LEA3: Mix 6, firing temperature 1340 °C.

Grain size distribution curves (Fig. 3) evidence that a larger amount of the 10–15 mm fraction occur in the aggregates LEA2 and LEA3; in LEA 2, such fraction reaches almost 80 wt.%. LEA1 is finer and more homogeneous (about 50 wt.% in the 7–10 mm fraction) and moreover its unit weight of particle is the lowest. This result is likely a consequence of a minor cohesion degree of the CaCO<sub>3</sub>-bearing crude grains, which may bring about disaggregation phenomena during the working phases before the firing process.

Table 7 compares the main physico-mechanical properties of LEAs with those of a common Italian commercial product (Leca and Lecastrutturale — LATERLITE SpA, Milan).

The LEA1 aggregate shows the lowest loose weight (467 kg/m<sup>3</sup>) and unit weight of particle (0.62 g/cm<sup>3</sup>). Quite close are the values referred to LEA2 and LEA3, the former slightly lower (515 vs. 555 kg/m<sup>3</sup> and 0.83 vs. 0.92 g/cm<sup>3</sup>). As far as strength of particles is considered, the best results were recorded for LEA3 (3.0 MPa) followed by LEA2 (2.9 MPa) whereas LEA1 gave very poor values (1.0 MPa). LEA2 is characterized by the best strength/unit weight of particle along with the lowest water absorption values after 24 hours.

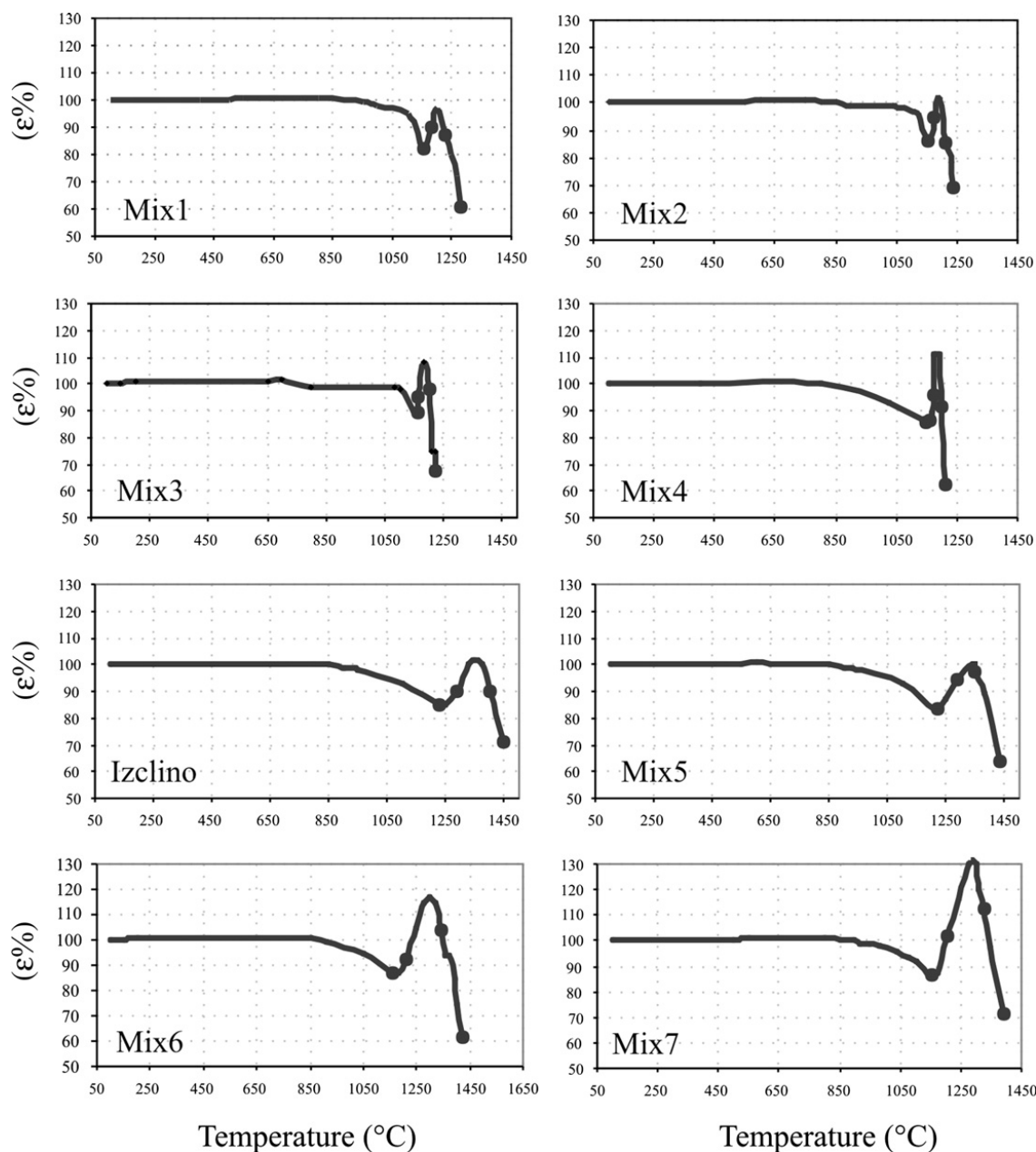


Fig. 2. Sintering curves for Izclino and mixtures.  $\epsilon\%$  is the height of the sample referred to the starting one (100% at 20 °C).

XRD analyses carried out on fired materials evidenced the glass as the main constituting phase for all the samples, with traces of quartz and feldspar as residual phases.

Fig. 4 reports macrographs of the aggregates. It can be observed that LEA2 and LEA3 (Fig. 4b and c, respectively) still show irregular shapes close to those of the unfired pellets, as a consequence of their low expansion. Unlike LEA2 and LEA3, aggregate LEA1 (Fig. 4a) loses the original shape thus assuming a spherical morphology, due to the high expansion. Furthermore, its external surface is affected by the presence of very small pores again as a consequence of the high expansion.

Internal sections of the aggregates (Fig. 5) observed under scanning electron microscope evidence the occurrence of two distinct microstructures: a system of large pores, with a maximum size depending on the kind of aggregate, and another made of smaller pores with constant dimension (ranging between 10 and 100  $\mu\text{m}$ ) for all the aggregates. In particular, LEA1 displays very large pores, even larger than 2 mm, forming a framework in which the smaller pore system developed (Fig. 5a).

The highest pore dimension in LEA2 (about 500  $\mu\text{m}$ ) still allows to distinguish the smaller pore system (Fig. 5b). As far as LEA3 is considered, it is quite

Table 4  
Characteristic temperatures (°C) observed on heating microscope

Mixture	$T_s$ Sintering temperature	$T_r$ Softening temperature	$T_f$ Melting temperature	$T_{me}$ Temp. max expansion
Mix 1: 65% Cab70, 30% DPM, 5% CP	1155	1180	1280	1200
Mix 2: 60% Cab70, 30% DPM, 10% CP	1155	1175	1240	1190
Mix 3: 55% Cab70, 30% DPM, 15% CP	1150	1165	1225	1185
Mix 4: 50% Cab70, 30% DPM, 20% CP	1160	1175	1215	1190
IZclino	1230	1285	1445	1355
Mix 5: 90% IZclino, 10% DPM	1205	1290	1435	1330
Mix 6: 70% IZclino, 30% DPM	1160	1210	1425	1300
Mix 7: 50% IZclino, 50% DPM	1155	1205	1390	1280

difficult to identify the above cited framework as larger pores do not exceed 350  $\mu\text{m}$ . Only the highest magnifications allow to distinguish zones of large and small pores (Fig. 5c and d).

Table 8 reports the features of mixtures and concretes C1, C2 and C3 obtained by LEA1, LEA2 and LEA3, respectively. The flow table test on sample C1 is only indicative as the mixture was poorly cohesive. Data obtained for C2 and C3 resulted within the expected

Table 6  
Firing tests on Cab70-CP mixtures, without DPM

Mixture	Mix (wt. %)		Unit weight of particle ( $\text{g}/\text{cm}^3$ )	
	Cab70	CP	Crude	Fired
A	95	5	1.20	1.29
B	85	15	1.20	1.53
C	70	30	1.20	1.38

values (UNI EN 12350-5, 2001). Water loss during the 28 days necessary to provide stiffness to the concrete (difference weight between fresh and dried volume) is lower than 15 g for all the samples. Bulk densities increase with the increase of the unit weight of particle of the aggregate. Concretes C2 and C3 show compressive strength values definitely higher than 30 MPa. The worst compressive strength value was recorded for C1 (about 27 MPa). SEM micrographs of concretes after the compressive strength tests show for C1 a discontinuity between the aggregates and the cement at places completely separated (Fig. 6a). A similar discontinuity is less evident in the C2 concrete (Fig. 6b). The best results were achieved for C3 (Fig. 6c) but no pieces of information are available to justify a possible interaction between aggregate and cement. An empirical observation was finally carried out by handily stressing the residue of concretes after the compressive strength test: aggregate and cement were easily separated in samples C1 and C2 whereas it was almost prohibitive for C3 concrete.

#### 4. Discussion

The use of natural zeolitized materials for the production of fired aggregates with unit weight of particle lower than 1  $\text{g}/\text{cm}^3$  requires firing temperatures close to

Table 5  
Firing tests in rotary kiln

	Mix formulation (wt.%)				Unit weight of particles ( $\text{g}/\text{cm}^3$ )				
	Cab70	IZclino	DPM	CP	1260 °C	1280 °C	1300 °C	1340 °C	1380 °C
Mix 0 <sup>a</sup>	70	–	30	–	0.98	–	0.81	–	–
Mix 1	65	–	30	5	1.10	1.01	0.8	–	–
Mix 2	60	–	30	10	0.98	0.83	0.62	–	–
Mix 3	55	–	30	15	1.01	0.83	0.65	–	–
Mix 4	50	–	30	20	1.04	0.77	0.61	–	–
IZclino	100	100	–	–	–	–	1.35	1.57	1.28
Mix 5	85	85	15	–	–	–	1.59	1.31	0.87
Mix 6	70	70	30	–	–	–	1.28	0.92	0.63
Mix 7	50	50	50	–	–	–	0.95	0.58	0.56

<sup>a</sup> de Gennaro et al. (2007).

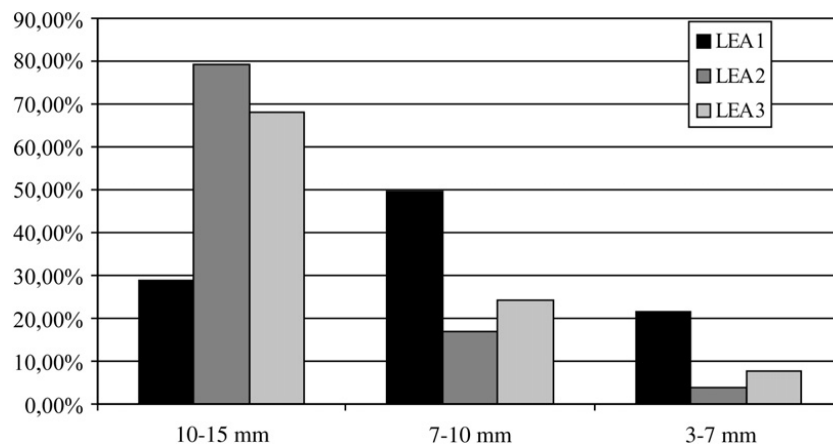


Fig. 3. Grain size distribution of lightweight aggregates.

1400 °C (de Gennaro et al., 2004). These data are confirmed by the present study which also evidenced that IZclino does not achieve expansion in rotary kiln at the investigated temperatures (max 1380 °C). Some tests demonstrate, however, that IZclino can expand, thus producing fired aggregates with unit weight of particle lower than 1 g/cm<sup>3</sup>, starting from 1420 °C. At any rate, it should be remarked that, in view of an industrial scale up, these temperatures are too high and economically inconvenient (e.g. expanded clays are industrially manufactured at temperatures not exceeding 1300 °C). Mixtures of IZclino and DPM can provide a suitable expansion already at 1300 °C (Table 5), thus confirming the results obtained with another zeolitized material such as Cab70 (de Gennaro et al., 2007). This behaviour is

likely to be due to a lower melting temperature of the polishing sludge (de Gennaro et al., 2007), which lowers the expansion temperature of the mixture (Table 4), and to the influence of SiC which, in presence of oxygen and starting from about 1000 °C, dissociates according to the following reaction:  $\text{SiC} + 2\text{O}_2 \rightarrow \text{SiO}_2 + \text{CO}_2$ . The gas amount produced during this reaction is definitely larger than that produced by the natural substances occurring in IZclino (mainly zeolitic water). This aspect promotes, together with temperature of reaction close to the softening point, a much greater expansion of the material.

The addition of CaCO<sub>3</sub> to Cab70-DPM mixtures favours the expansion during the firing process and a consequent decrease of the unit weight of particle (Table 5). CP in the mixture seems to play mainly the role of a low melting agent, since it did not give rise to any expansion when added to Cab70 without DPM (Table 6).

The different physico-mechanical features of the aggregates LEA1, LEA2 and LEA3 (Table 7) should be related to the internal and external structures of single grains (Fig. 5). In particular, the larger pores of LEA1 make this sample less dense and with a lower mechanical strength compared to LEA2 and LEA3. In contrast, LEA3 has the best mechanical properties due to its pore size homogeneity. In general terms, it can be assessed that properties of LEA1 are close to those of a common commercial product (classic Leca expanded clays) whereas LEA2 and LEA3 exhibit values ranging between those of Leca and other more dense and resistant commercial products (Lecastrutturali) (Table 7).

All the investigated aggregates have water absorption values that are lower than those referred to the above reported commercial expanded clays. Slightly higher water absorption of LEA1 could be due to the presence of small pores on the glassy surface, as described in the previous paragraph (Fig. 4).

Table 7

Technical features of lightweight aggregates compared with those of some commercial expanded clays (Leca®, produced and traded in Italy by Laterlite — Milano)

Lightweight aggregate	LEA1	LEA2	LEA3	Leca	Leca	Lecastrutturale
Grain size (mm)	3–15	3–15	3–15	3–8	8–12	3–15
Unit weight of particle (g/cm <sup>3</sup> )	0.62	0.83	0.92	<0.6	<0.6	1.3
Loose weight (kg/m <sup>3</sup> )	467	515	555	380	340	770
Water absorption (wt.%)	3.1	1.2	2.5	11	11	>7
Strength of particles (MPa)	1.0	2.9	3.0	1.5	1.0	4.5
Strength/unit weight of particles	1.58	3.54	3.26	2.31	1.67	3.46



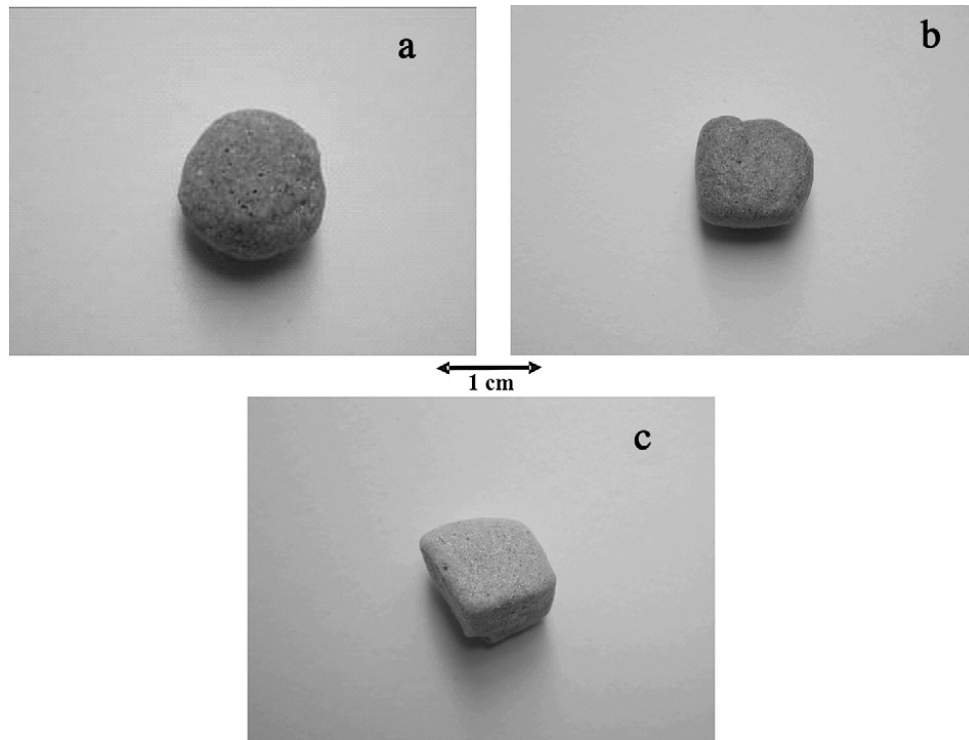


Fig. 4. Macrographs of the external structures of aggregates LEA1 (a), LEA2 (b) and LEA3 (c).

The differences in mechanical properties of the lightweight aggregates also affect technical properties of concrete specimens. Therefore, best results were

obtained using aggregates LEA2 and LEA3 compared to concretes manufactured with LEA1 (Table 8). It cannot be ruled out, however, that the different behaviour of the

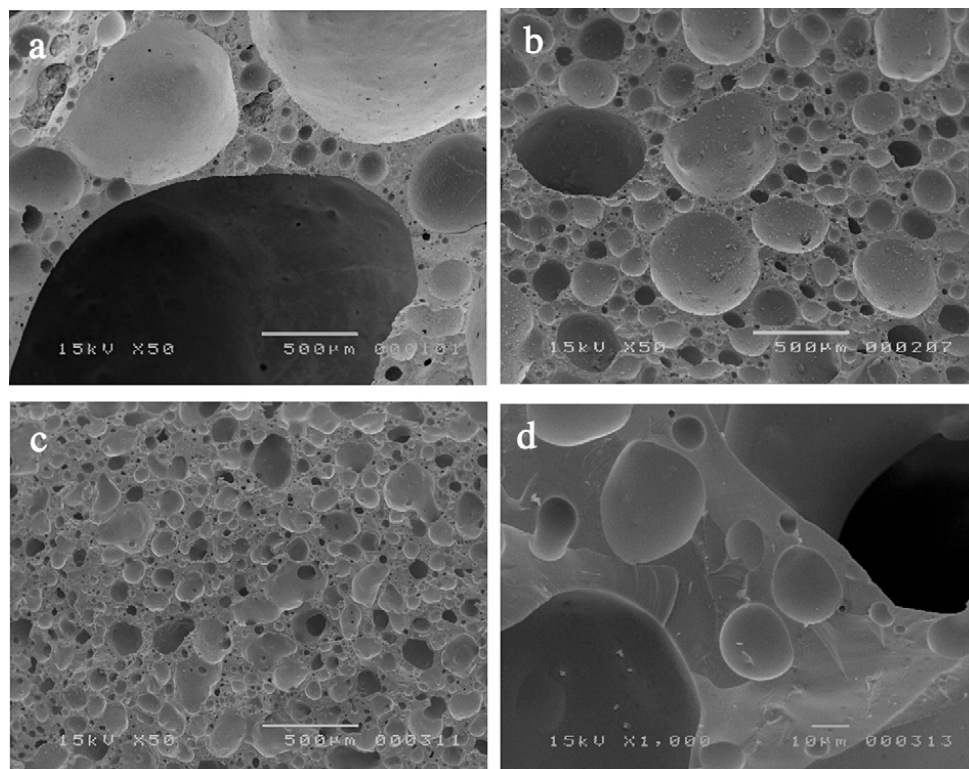


Fig. 5. SEM micrographs of the internal structures of aggregates LEA1 (a), LEA2 (b), and LEA3 (c and d).

Table 8

Some features of mixtures and concretes produced with LEA1, 2 and 3 aggregates

Specimen	Flow table test	Fresh bulk density	Hardened bulk density	Compressive strength
	%	kg/m <sup>3</sup>	28 days kg/m <sup>3</sup>	MPa
C1	30	1775	1762	27.5
C2	40	1780	1773	32.7
C3	50	1805	1800	34.2

three concretes is due also to a different degree of interaction between aggregate and cement, as evidenced by the SEM observations (Fig. 6). The concrete C1, showing the worst features, has large discontinuities between aggregate and cement; on the other side concrete C3, with the highest strength of particles, shows much better structural properties.

Bulk density of the hardened concretes is slightly lower than those measured on fresh concretes. This positive result, obtained by leaving concretes to harden in saturated conditions, suggests that most water added to the mixture was used for the hydration of calcium silicates and aluminates constituting the clinker. Experimental data suggest that, as far as bulk density and compressive strength after 28 days are concerned, aggregates LEA2 and LEA3 can be used to manufacture structural lightweight concretes, the latter being the most performing. In fact, using the mixture reported in Table 1, which provides for doses of 350 kg/m<sup>3</sup> of CEM II/A-LL 42,5R cement and an acrylic superfluidificant additive (1.3 l/100 kg of cement), it is possible to obtain a concrete with a characteristic compressive strength of 25 MPa (Suppl. Ord. G.U.R.I. n° 29, 1996a).

Aggregates LEA1, showing technical features more similar to those of Leca expanded clays, are suitable for a possible use in the production of thermo-insulating lightweight concretes that are lightweight concretes with a bulk density between 300 and 800 kg/m<sup>3</sup> and compressive strength ranging between 0.5 and 7 MPa (Collepari, 2002). These concretes are generally used as filling materials or as insulating coatings.

## 5. Conclusion

This research provides further proofs of the possible use of zeolitized natural products for the production of Lightweight Expanded Aggregates (LEAs). In particular, it was assessed that the addition of a SiC-bearing industrial waste (DPM, porcelain stoneware polishing sludge) in 70% zeolite-30% sludge mixtures provides

expanded aggregates suitable for the manufacture of lightweight structural concretes. These results can be obtained using either a phillipsite/chabazite-rich tuff (Campanian Ignimbrite — Cab70) or a clinoptilolite-rich epiclastite (Turkish epiclastite — IZclino), even though the latter requires a slightly higher firing temperature (1340 °C instead of 1300 °C generally used for Cab70). A further addition to the mixture (10 wt.% of calcium carbonate, CP, replacing the zeolitized material) allows to manufacture expanded

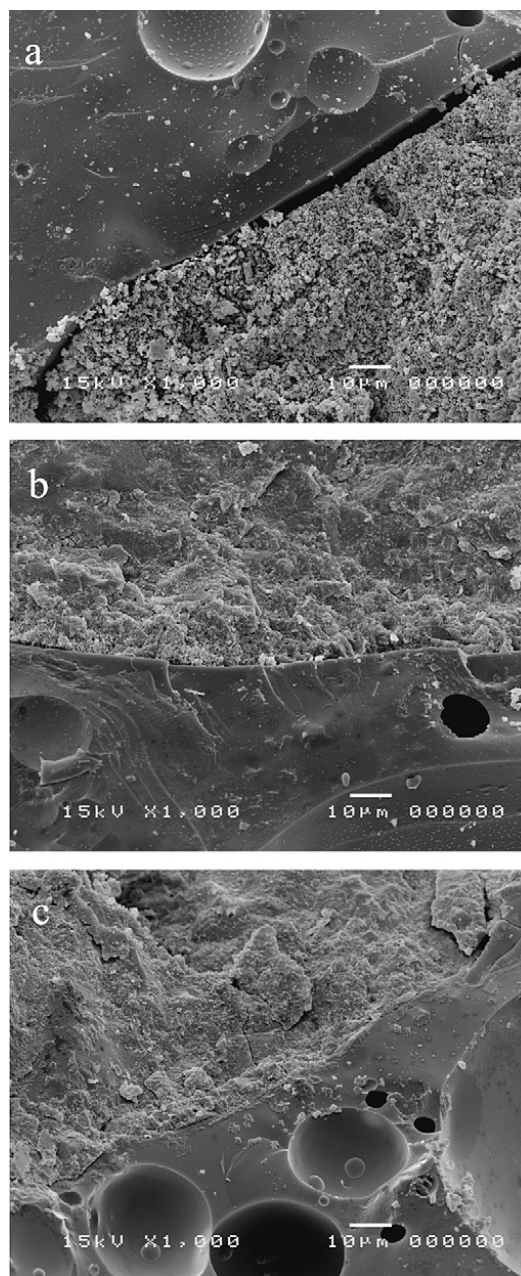


Fig. 6. Aggregate-cement boundary in concretes C1 (a), C2 (b) and C3 (c).



aggregates with technical features close to those of commercial expanded clays. In particular, the mixture made of 60% Cab70+30% DPM+10% CP allows to produce aggregates with very low unit weight of particles ( $0.62 \text{ g/cm}^3$ ) and it is suitable to manufacture lightweight concretes characterized by high thermal and acoustic insulation. Moreover, the use of the above mentioned mixtures for the production of lightweight aggregates turns to be mostly interesting if account is taken of the low cost of raw materials. As far as the polishing sludge is concerned, it should be remarked the double advantage of its use in terms of provisioning costs and reduction of environmental impact for tilemaking companies which are currently facing disposal costs and stricter environmental regulation. Finally, it should be remarked that the annual output of this sludge (50,000 tons in 1999 but now fastly increasing) could not even fulfill the demand of a single plant producing 200,000  $\text{m}^3$  per year of lightweight aggregates. Such a kind of production would require about 100,000 tons of raw materials. The combined use of this waste (30%) with zeolitized materials (70%) would reduce the annual requirements of sludge to about 30,000 tons, thus within the amount produced yearly. As far as zeolite-rich materials are considered, it is important to remark that they have a very low commercial cost and are widespread over the national territory. Furthermore, it can also represent a waste material after sewing operation of dimension stones in quarry or as separated fine fraction during sieving processes for the production of granulated zeolite.

The results of the present research shed light on new perspective uses of zeolitized materials and polishing sludge. However, further studies are required to widen the knowledge on this specific aspect, mainly aimed at increasing the laboratory production of lightweight aggregates which could allow an exhaustive characterization of both aggregates and concretes. Finally, the promising results obtained with the polishing sludge suggest to test also other wastes with similar chemical composition ( $\text{SiO}_2 > 50\%$ ;  $10\% < \text{Al}_2\text{O}_3 < 20\%$ ;  $10\% < \text{fluxing} < 20\%$ ; always bearing SiC) such as sludges from polishing of granites and/or lavas.

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