Clayey Diatomite from a Deposit in Central Greece – A Multifunctional Raw Material for Absorption and Insulation

G.N. Georgiades* and M.G. Stamatakis**

A sedimentary Upper Miocene succession discovered in Central Greece is mainly composed of clay minerals and diatom frustules. Homogeneous, fine-grained material found in layers over 40 m thick was chemically and mineralogically characterized, and then tested on laboratory and semi-industrial scale as raw material for absorbents and for the production of insulation bricks and lightweight aggregates (LWA). The results obtained were promising for all the applications tested. The reserves of the sedimentary rock are estimated at several million tonnes, sufficient for mining operations for all three applications over a period of more than 20 years.

*) *Dr G.N. Georgiades*
KTIMET SA
Thessaloniki, Greece

**) *Professor M.G. Stamatakis*
National & Kapodistrian University of Athens
Department of Geology & Geoenvironment
15784 Athens
Greece

Corresponding author: M.G. Stamatakis
stamatakis@geol.uoa.gr

Keywords: raw material, clayey diatomite, absorption, lightweight, aggregates, insulation

1 Introduction

During the implementation of basic research and several R&D projects on the suitability of the diatomaceous rocks of Greece for several industrial applications, a significant deposit with a special mineralogical composition was located in Thessaly, Central Greece [1–9]. This diatomaceous material was successfully tested for the production of industrial absorbents, lightweight aggregates (LWA) and lightweight insulation bricks. The analyses and tests were conducted on laboratory and semi-industrial scale in Greece, Belgium, France and the USA.

2 Geology

In a sedimentary basin of Upper Miocene age, located northwest of Larissa, Thessaly, Central Greece, a thick yellowish to off-white clayey diatomite succession developed, covering an area of more than 10 km² [10 – 12].

According to borehole data, the cumulative thickness of the succession is more than 40 m (Figs.1, 2, 3). The substrate of the basin consists of Mesozoic metamorphic rocks. Two representative bulk rock samples weighing several tonnes each were collected from the Eastern (GRE-1) and the Western (GRE-2) part of the basin.

3 Characterization of the raw materials

3.1 Analytical techniques

The mineralogical and chemical analyses were performed in the analytical laboratories of *World Industrial Minerals, CTL Group (USA)* and the *University of Athens*. The mineralogy of the samples was established with the use of X-ray diffraction (XRD) analysis (crystalline phases) and scanning electron microscopy (SEM) analysis for the amorphous phase (diatomaceous silica). The main elements were measured by wet chemical analysis. The technical measurements were

Fig.1 Location map of the studied area

performed by *BRGM* (France) and *INISMA* (Belgium]).

3.2 General mineralogy

After analysing more than 70 reconnaissance, borehole and bulk rock samples from the entire basin, it was found that the clayey diatomite is richer in clay content in the Western part of the basin (bulk sample GRE-1), whereas the Eastern part of the basin is

Fig. 2 Extraction of the bulk sample GRE-2 at the eastern part of the basin, the run of mine samples are wet and dark coloured

Fig. 3 When wet, the clayey diatomite looks brownish, turning to off-white by drying

Tab. 1 Mineral analysis of the Greek clayey diatomite

Sample	Mineral						
	Qtz	Verm	Sm	oA	Ill	Fl	Chl
GRE-1	TR	**MJ**	**MJ**	**MJ**	TR	MD	MD
GRE-2	TR	MD	MD	**MJ**	TR	MD	TR

Explanatory notes: Qtz = quartz, Verm = vermiculite, Sm = smectite, oA = opal-A, Ill = illite, Fl = feldspars, Chl = chlorite. MJ = major, MD = moderate and TR = minor or trace constituent

richer in opaline silica, namely diatom frustules (bulk sample GRE-2).

3.3 Detailed mineralogy

The main characteristic features of the clay-rich diatomaceous rock are:

- its high content of biogenic amorphous silica, represented mainly of disk-shaped and cylindrical diatom frustules with the form of opal-A (Fig. 4a –d)
- the presence of minor amounts of detrital quartz and feldspar and the absence of any carbonate minerals
- its clay mineralogy which includes expanded clays of the smectite group, illite, chlorite and vermiculite.

Generally, the mineralogy of the specific diatomite deposit has similarities to the Danish Moler.

The results of the mineral analysis are given in Tab. 1. The quartz content of sample GRE-1 was determined to be as low as 1 % [Rietveld method]. For sample GRE-2 the crystalline silica phases were measured by *World Industrial Minerals,* Colorado, USA. According to these measurements, the only detectable silica polymorph is a low quartz content (~5 %), whereas other crystalline phases such as cristobalite and/or tridymite are absent. The amorphous (biogenic) silica phase content is high, reaching 77 % of the total silica, the rest being fixed in the aluminosilicate minerals present.

3.4 Chemistry

The chemistry of the samples was measured by wet chemical analysis (*World Industrial Minerals, CTL Group*, USA). The results are shown in Table 2.

Besides silica, alumina and iron oxides are the main phases of the rock. The low CaO

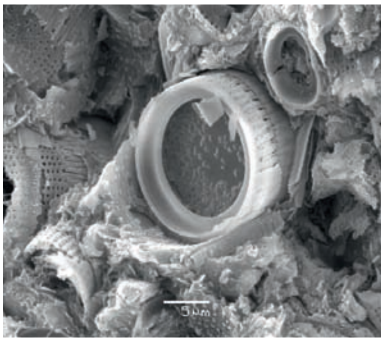

Fig. 4a SEM image of cylindrical diatom frustules that retain their minute structure, sample from the eastern part of the basin

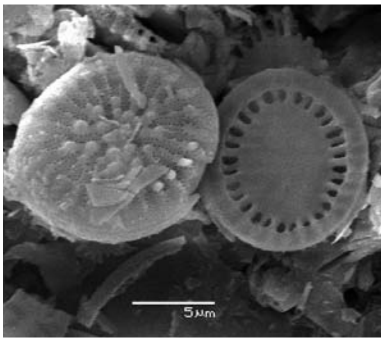

Fig. 4b SEM image of disk-shaped diatom frustules, sample from the western part of the basin

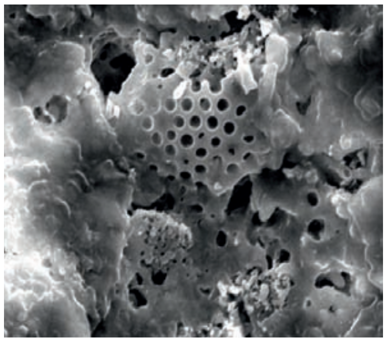

Fig. 5 SEM image of the calcined clayey diatomite (~800 °C) for the production of absorbents; relics of diatoms are visible (NKUA)

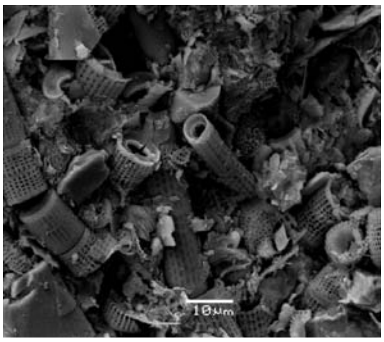

Fig. 4c Colonies of cylindrical diatom frustules not affected by silica diagenesis, site GRE-1, western part of the basin

Fig. 4d Colonies of cylindrical diatom frustules not affected by silica diagenesis, site GRE-1, western part of the basin

Fig. 6 Calcined product in granules 0,3 – 1,7 mm

Tab. 2 Chemical analysis of the Greek clayey diatomite

Component	GRE-1	GRE-2
Na_2O	1,28	0,68
K_2O	2,58	1,85
CaO	1,82	1,03
MgO	1,79	1,52
Fe_2O_3	8,08	4,88
Al_2O_3	17,83	13,12
SiO_2	59,52	69,49
LOI	7,37	5,59
Total	100,27	98,16

Tab. 3 Technical properties of the material GRE-2

Westinghouse oil absorption (BRGM)	113 %
Westinghouse water absorption (World Industrial Minerals)	153,50 %

Tab. 4 Measurements of the oil absorption of the Greek clayey diatomite, after NF V 19-002 method, in comparison with industrial absorbents (BRGM – France standards and comparison tests)

Material	Oil absorption* [%]
Greek diatomite	111–115
Danish diatomite	93–97
Attapulgite	54–55
Montmorillonite	86–88
Chinese diatomite	118–120

* Motor oil ESSO Extra SAE 20W50

Fig. 7 Pilot crushing – feeding device

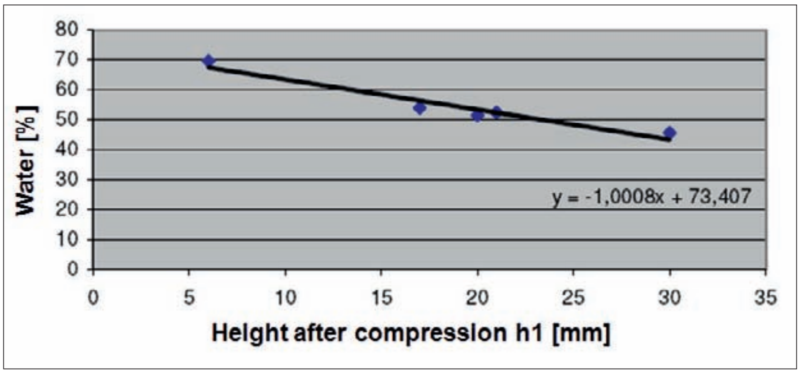

Fig. 9 Plasticity characteristics of the samples

Fig. 8 Pilot crushing – screening -10 mm

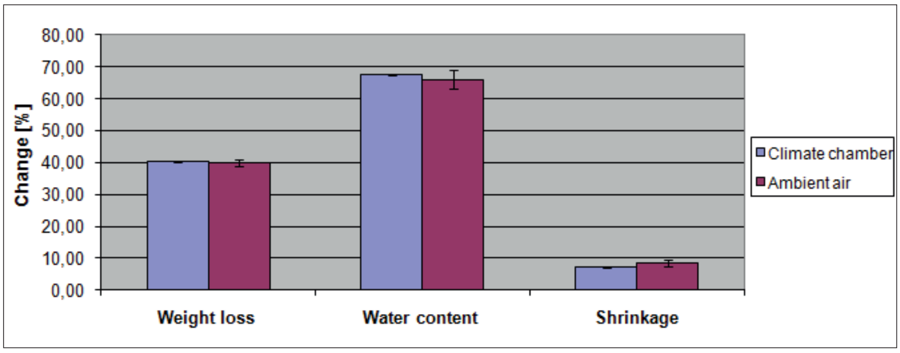

Fig.10 Drying characterization of the extruded parallel-epiped samples (rectangular section 25 mm × 30 mm)

and MgO contents of the clayey diatomite reflect the absence of carbonates.

4 Applications

Both bulk samples were tested for three main applications: Absorbents for chemicals and oils (*Centre Terre & Pierre*, Belgium), lightweight insulation bricks (*Institute National Interuniversitaire des Silicates Sals et Materiaux – INISMA*, Belgium), lightweight aggregates (*NKUA*, Athens).

4.1 Absorbents for chemicals and oils

It is known that absorbents for chemicals and oils have to be in granulated form (commonly 0,3 – 1,7 mm) and to contain a low percentage of fines (max. 2 % < 0,3 mm). The absorbents have to have enough mechanical resistance to eliminate the percentage of fines for health and environmental reasons, and they must have maximum absorbing capacity.

Both parameters are influenced by the raw material's mineralogy and the calcining temperature. By testing the two bulk samples it was found that the opaline silica-rich GRE-2 sample has given the best results (Fig. 5). The mechanical strength of the product tested in practice by the French absorbents trade Company OLLAG, France, achieved good results.
For evaluation, GRE-2 material was ground, calcined and screened to 0,3 – 1,7 mm on

semi-industrial scale (Figs. 6, 7, 8). The final product has significant absorbing capacity (Table 3). Using ESSO Extra SAE 20W50 motor oil (procedure NF V 19-002, corresponding to the Westinghouse method), the Greek Moler absorbing capacity is higher or comparable with commercial reference samples (comparisons at BRGM-France, see Table 4).
The mechanical strength of the product tested in practice by the French absorbents trade company *OLLAG*, France, achieved good results.

4.2 Insulation bricks

Extensive trials were performed by *INISMA* (Belgium) on the GRE-2 material for the production of lightweight fired construction blocks. Parameters that were examined in calcined material of various firing temperatures were: plasticity, extrusion, drying, weight loss, shrinkage, apparent and true density, porosity by Hg porosimetry, water sorption, texture examination by microscopy and compressive strength of the final product. The properties obtained after firing the material at 900 °C rank between commercial cellular concrete blocks and commercial (extruded) clay hollow blocks fired at 950 °C. The results are presented in Tab. 5.
The clayey diatomite is used without any additives and a classical manufacturing route is followed: blending – extrusion – drying – firing.
The working program was as follows:

- Plasticity test according to Pfefferkorn
- Extrusion of 70 parallelepipedons with rectangular cross section (25 mm x 30 mm)
- Controlled drying of 5 parallel epipedons in climate chamber
- Uncontrolled drying of the other parallel epipedons in ambient conditions with recording of weight loss and shrinkage
- Firing of 3 series of 20 samples each at temperatures: 600, 700, 800, 850, 900 and 950 °C in electrical kiln (normal air atmosphere) with recording of weight loss and shrinkage
- Hydrostatic measurement of apparent density (3 x 5 samples)
- Measurement of water sorption by immersion (3 x 5 samples)
- Measurement of compressive strength in to 2 directions (5 samples // and 5 samples ⊥ µto extrusion direction) including rectification of 3 x 10 samples.

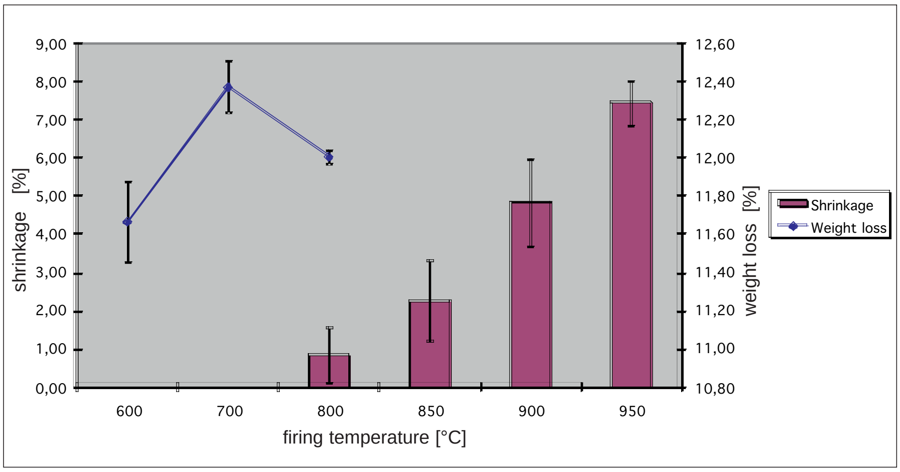

Fig. 11 Shrinkage and weight loss of the samples fired at gradient temperatures in electrical kiln (air atmosphere)

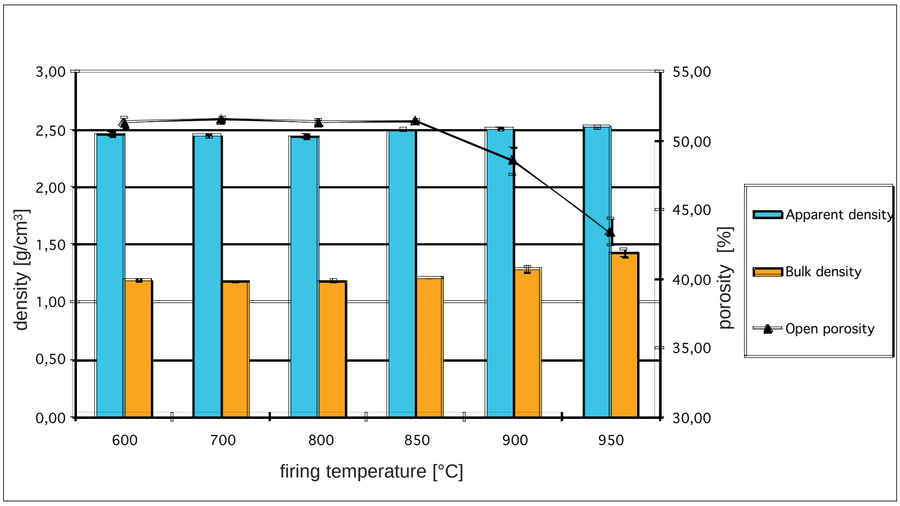

Fig. 12 Densities (bulk and apparent) and porosity of the samples fired at gradient temperatures in electrical kiln (air atmosphere). The gradient heating program used was: 20 – 600 °C, 150 °C/h; 600 – 950 °C, 200 °C/h; duration at 950 °C for 3 h; 950 – 600 °C, 200 °C/h; 600 – 500, 50 °C/h; 500 – 20 °C free

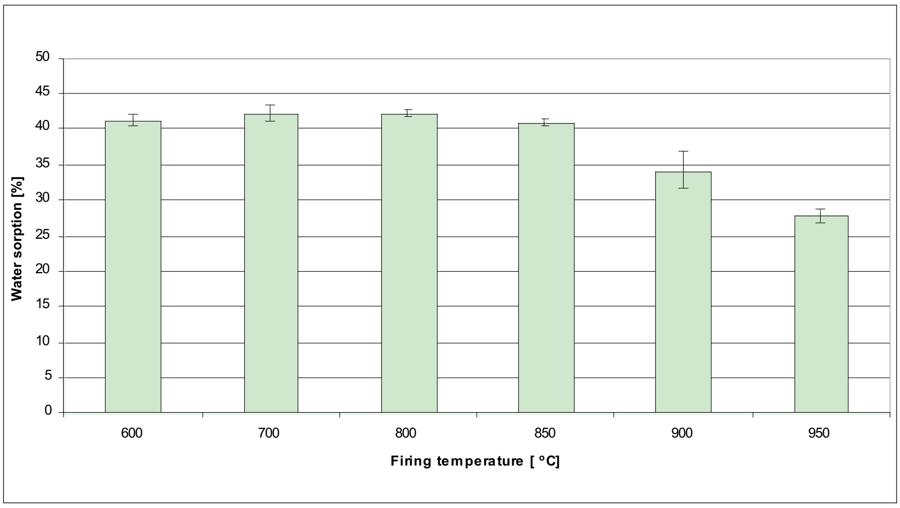

Fig. 13 Mean water sorption after 24 h immersion

Tab. 5 **Drying characterization of the samples**

Material	Cellular block	GRE-2	Hollow block
Bulk density [g/cm³]	0,4–0,5	1,3	1,8
Water sorption [%]	-	34	13–16
Compressive strength [N/mm²]	3	22–30	25

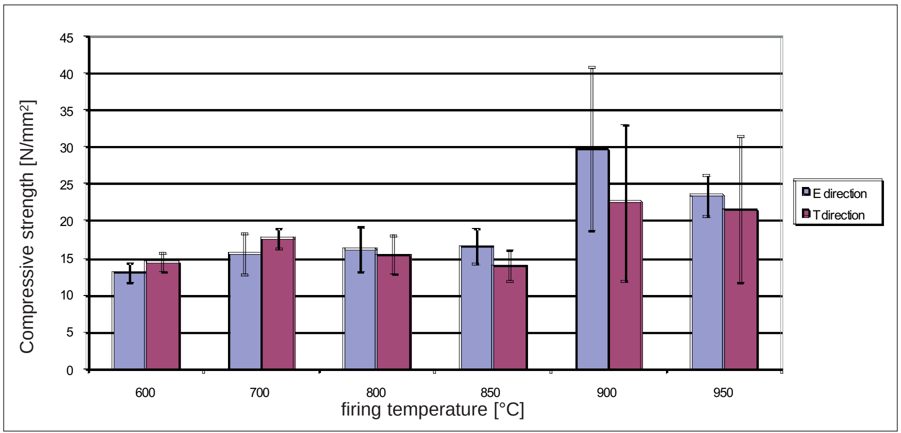

Fig. 14 **The compressive strength of the fired samples measured on 19,3-mm diameter cylinders in the extrusion direction and perpendicular to it (E and T directions respectively).**
-- In this batch of samples many ruptures have been observed during boring and machining

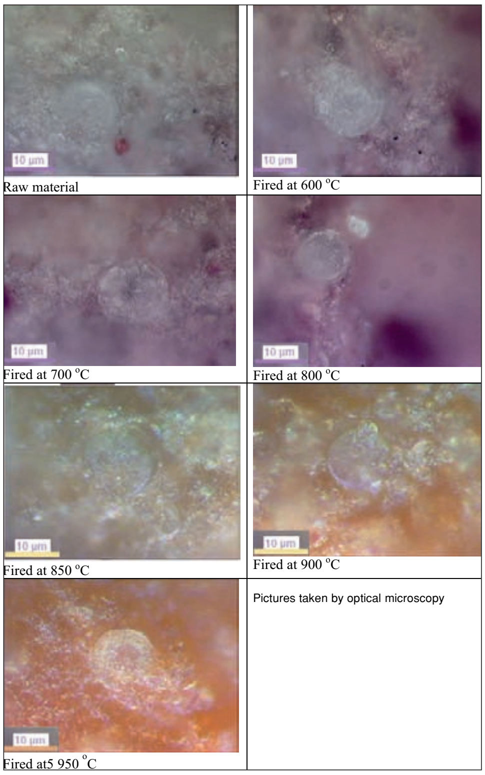

Fig. 15 **CCD images coupled with a light microscope of the diatom frustule-rich raw material fired at different temperatures**

4.2.1 Plasticity test according to Pfefferkorn

According to Pfefferkorn, the plasticity of clay is deduced from the compression ratio "a" (a = h0 / h1, where h1 is the height after compression and h0 the initial height = 40 mm) of a cylindrical sample under well-defined conditions. The samples are prepared according to various water contents. When the height loss of the sample is 70 % of the initial height, the water content is considered right for good plasticity.

The correct plasticity index is calculated for h1 equal to 12 (a = 33). In Fig. 9 one can see that h1 = 12 corresponds to 61,4 % water. The workability index is calculated for h1 = 16 (a = 2,5), as good workability must be 2,5 < a < 4, which corresponds 57,4 % water. In our experimental conditions, 74,8 % was used for the extrusion of the parallel epipedons.

4.2.2 Controlled drying in climate chamber

From the 70 extruded parallel epipedons, 5 have been dried in a climate chamber, with recording of weight loss and shrinkage, to characterize the resistance to cracking. The results are shown in Fig. 10.

One can see from these results that the weight loss and shrinkage are homogeneous among the 5 samples. The water content, lost during drying, is near to the water added to the samples for extrusion. The shrinkage seems quite normal for a clayey sample.

Eleven other samples have been dried in ambient air, with recording of weight loss and shrinkage, also to characterize the resistance to cracking (Fig. 10). One can see that when allowing the samples to dry in ambient air, the water loss corresponds to the water content of the samples. The linear shrinkage seems to vary between 7 and 10 %.

4.2.3 Firing

A series of 6 samples have been fired each at 6 temperatures (600, 700, 800, 850, 900 and 950 °C) in an electrical kiln (normal air

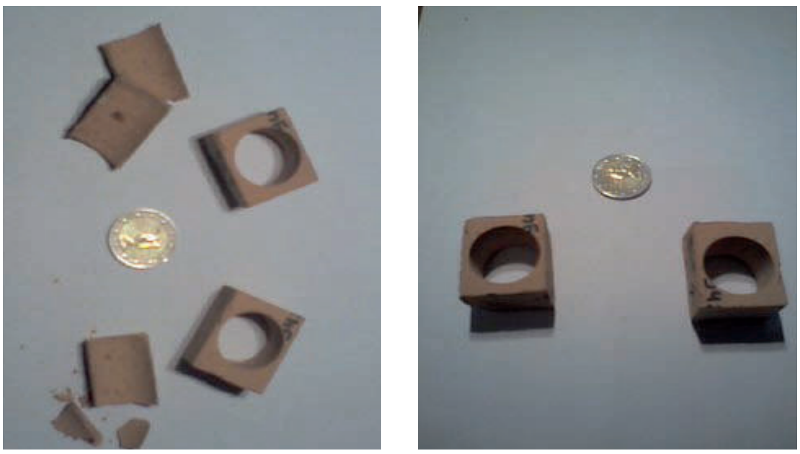

Fig. 16a + b **Laboratory produced bricks, after technical trials**

Fig. 17 **LWA before (white) and after (brown) burning**

Fig. 18 **Production of LWA in a laboratory furnace**

atmosphere) with recording of weight loss and shrinkage (Fig. 11). The results are shown in Tab. 6. The firing cycle was as follows:

- *Recording weight loss*

A mean weight loss of 11,67, 12,37 and 12,01 % is observed after firing at 600, 700 and 800 °C, respectively.

- *Recording shrinkage*

No shrinkage is observed when firing at 600 and 700 °C, and minor shrinkage up to 1,4 % is observed when firing at 800 °C. From 850 °C, the shrinkage increases to between 1,4 and 8 % of the initial length. At 900 °C, the shrinkage is quite acceptable.

4.2.4 Hydrostatic measurement of densities and porosity

Hydrostatic measurements of bulk and apparent densities, and open porosity have been carried out after full vacuum on 3 series of samples fired at 600, 700 and 800 °C. The results are shown in Fig. 12. After firing at 600, 700 and 800 °C, no important difference is observed either in the density values or in porosity.

Porosity has been measured as being about 51 %. When firing above 800 °C, and especially at 900 and 950 °C, density and porosity values start to increase. At 950 °C, porosity becomes less interesting from an insulating point of view.

The water sorption of the fired samples is shown in Fig. 13. The mean water sorption at 600, 700, 800 and 850 °C is 41,22 %, 42,25 %, 42,31 % and 40,87 % after 48 h immersion. It starts to decrease significantly when firing at 900 and 950 °C.

4.2.5 Compressive strength

The compressive strength (Fig. 14) has been measured on 19,3-mm-diameter cylinders in the extrusion direction (E) and perpendicular to it (T). Up to 850 °C, the compressive strength in both directions varies between 13 and 17 N/mm^2. From 900 °C it increases twice in the extrusion direction, which is very interesting.

4.2.6 Discussion of the analytical results

As shown in Table 5, key properties of the Greek diatomite material fired at 900 °C, such as bulk density, water sorption and compressive strength, rank between commercial cellular concrete blocks and commercial (extruded) hollow blocks.

Nevertheless, it appears that the clayey diatomite material has higher compressive strength than the other materials with very good lightweight and insulating properties. This last property could be quantified at a later stage by thermal conductivity measurements on the three types of materials.

Remark: Bulk density and compressive strength of the hollow blocks in the Tab. 5 are figures calculated from the *INISMA* data sheet, taking into account that the area occupied by the holes is about 50 % of the total area perpendicular to the extrusion direction.

4.2.7 Optical microscopy

Several images of the raw material and fired products were taken using a CCD coupled to an optical microscope, to check the behaviour of the diatomite texture at each firing temperature (Fig. 15, *INISMA* Labs).

Due to melting phenomena, the detailed minute structure of the diatom frustules starts to collapse from 900 °C, but the brick structure stays intact.

4.3 Lightweight aggregates

Lightweight aggregates (LWA) are minerals, rocks, products and by-products that are used as bulk fillers in lightweight structural

Fig. 19 **LWAs produced by the Greek clayey diatomite just pulled out from the furnace (NKUA)**

Fig. 20 **The cooled LWAs obtain a reddish colour and the characteristic porous structure (*NKUA*)**

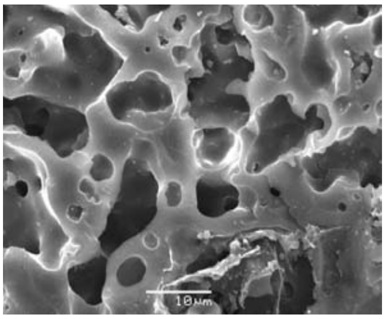

Fig. 21 **SEM images of the LWAs produced with the Greek moler; the honeycomb structure is visible (*NKUA*)**

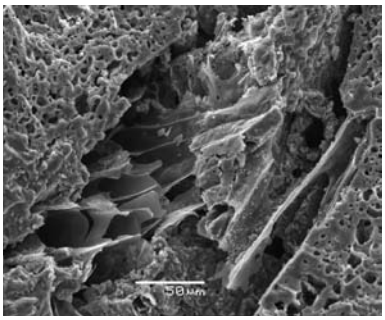

Fig. 22 **SEM images of the LWAs produced with the Greek moler; the glassy phase predominates (*NKUA*)**

concrete, building blocks, precast structural units, road surfacing materials, plaster aggregates, loose insulating fill, gardening, geotechnical applications and insulation.

The clay- and opal-A-rich bulk samples from the area under investigation were tested for the production of LWA. The following experimental procedures were included: sample preparation, wet mixing (water/solids 1/2), of the dried/milled raw material (95 %) with sawdust (5 %), pelletizing to pellets of 0,5 – 2,0 cm in diameter and calcination of the pellets at ~1120 °C for 15 min (Figs. 17–20).

The resulting lightweight aggregates are highly porous, with a specific gravity of 0,55 – 0,75 g/cm³ and compressive strength (fracture load) up to 2000 g/mm². The textural analyses of the sintered products revealed the presence of series of micro-pores 2 –100 µm in size with a honey-comb structure in the interior of the aggregates, whereas their outside surface has closed porosity (Figs. 21, 22).

The LWAs produced at the laboratory using the Greek clayey diatomite have apparent density and compressive strength similar to commercial LWAs from Denmark and Germany [13, 14]. Current research in other sites of the region indicates that the Neogene sedimentary rocks of the area that lies Northwest of the town of Larissa has significant potential for the development of the Central Greece clayey diatomite as LWA raw material.

5 Reserves

By carrying out extensive comparative tests in order to find the optimum clayey diatomite for the investigated applications, a suitable area of several hundred thousand square metres in the given basin was located, in which the exploitable reserves are estimated to several million tonnes, a tonnage that is sufficient for mining operations for all three applications over a period of more than 20 years [15].

6 Future plans

A feasibility study for an absorbent production plant is currently being conducted. Extensive field work at several locations in the country, in conjunction with the laboratory data on certain diatomite types identified in Greece, revealed that the Larissa deposit is the only exploitable clayey diatomite deposit in Greece so far.

Acknowledgements

Thanks are expressed to *Mr. Chris Spencer* (Consultant / UK) and to *Mr. Kostas Chatzicharalampous* (mining engineer) for their assistance in the utilization of the Greek clayey diatomite.

We also thank *George Stamatakis* (MSci Chemist) for his assistance in presenting the results with graphs. Part of the results of the current paper has been presented in the IM19 meeting that was held in Athens in March 2008.

References

[[1] Stamatakis, G.; Dermitzakis, M.D.; Economou-Amilli, A.; Magganas, A.: Petrology and diagenetic changes in Miocene marine diatomaceous deposits from Zakynthos Island, Greece. In: Hein, J., & Obradovic, J. (Eds.): Siliceous deposits of Tethys and Pacific regions. New York Springer Verlag (1988) 130–139

[2] Stamatakis, M.G.; Magganas, A.: Thermally induced silica transformation in Pliocene diatomaceous layers from Aegina Island, Greece. In: Hein, J., and Obradovic, J. (Eds): Siliceous deposits of Tethys and Pacific regions. New York Springer Verlag (1988) 141–150

[3] Stamatakis, M.G.; Hein, J.R.; Magganas, A.: Geochemistry and diagenesis of Miocene lacustrine siliceous sedimentary and pyroclastic rocks, Mytilinii basin, Samos Island, Greece. Sedimentary Geology 64 (1989) 65–78

[4] Stamatakis, M.G.; Calvo, J.P.; Regueiro, M.; Bellanca, A.; Neri, R.: Alternating diatomaceous and volcanoclastic deposits in northern Milos Island, Aegean Sea, Greece. 15th International Sedimentology Congress, Alicante 1998, Book of Abstracts (1998) 738–739

[5] Triantaphyllou, M.V.; Tsaparas, N.; Stamatakis, M.G.; Dermitzakis, M.D.: Calcareous nannofossil biostratigraphy and petrological analysis of the pre-evaporitic diatomaceous sediments from Gavdos Island, southern Greece. N. Jb. Geol. Palaont. Mh. (1999) [3] 161–178

[6] Bedelean, I.; Ivan, I.; Stamatakis, M.G.; Duca, V.; Pop, D.; Bedelean, H.; Korpos, H.; Racatoian, P.: The production of synthetic wollastonite and diopside by using silica-rich natural raw materials. Tile and Brick International (2000) [2] 82–87

[7] Stamatakis, M.G.; Fragoulis, D.; Csirik, G.; Bedelean, I.; Pedersen, S.: A study on the properties of blended cements produced with biogenic micro-silica-rich rocks. 36th Forum on the Geology of Industrial Minerals, Bath, England 5–12 May 2000, Camborne School of Mines, Cornwall, UK, Proceedings (P.W. Scott and C.M. Bristow, Eds.), (2000) 359

[8] Fragoulis, D.; Stamatakis, M.G.; Csiric, G.; Papageorgiou, D.: Diatomaceous earth as a cement additive – a case study of deposits for Greece and Hungary. ZKG International 55 (2002) [1] 80–85

[9] Stamatakis, M.G.; Fragoulis, D.; Csiric, G.; Bedelean, I.; Pedersen, S.: The influence of biogenic micro-silica-rich rocks on the properties of blended cements. Cement & Concrete Composites 25 (2003) 177–184

[10] Stamatakis, M.G.; Koukouzas, N.K.: The occurrence of phosphate minerals related with lacustrine clayey diatomite deposits, Thessaly, Central Greece. Sedimentary Geology 139 (2001) 33–47

[11] Stamatakis, M.G.: Phosphate deposits of Neogene age in Greece: Mineralogy, geochemistry and genetic implications. Chemie der Erde 64 (2003) 329–357

[12] Stamatakis, M.G.: Characterization of biogenic amorphous silica deposits in Greece and their industrial potential. In: Mineral Exploration and Sustainable Development (D.G. Eliopoulos et al., Eds.) Millpress, Rotterdam, Netherlands 2 (2003) 927–930

[13] Fragoulis, D.; Stamatakis, M.G.; Chaniotakis, E.; Columbus, G.: Characterization of lightweight aggregates produced with clayey diatomite rocks originated from Greece. Materials Characterization 53 (2004) 307–316

[14] Fragoulis, D.; Stamatakis, M.G.; Chaniotakis, E., Columbus, G.: The utilization of clayey diatomite in the production of lightweight aggregates and concrete. Tile and Brick International 19 (2003) [6] 392–397

[15] Georgiades, G.; Stamatakis, M.G.; Chatzicharalampous, K.: The Greek clayey diatomite: a multifunctional industrial rock for absorption and insulation. 19th International Congress on Industrial Minerals, March 2008, Athens, 5 pp.