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Thermal conductivity of lightweight aggregate based on coal fly ash

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Abstract The article presents the results of physical and chemical properties of lightweight aggregates (LWA) obtained by the thermal treatments of raw composition based on fly ash, supplied by electric plants from Serbia. The production process of LWA consists of raw material preparation, plastic shaping–extrusion, granulation, and thermal treatment at three temperatures: 1100, 1150, and 1200 °C. The final firing temperature ($T = 1150$ °C) is chosen based on the mechanical and physical properties of the designed aggregates. The particle-size distribution of the LWAs is unimodal ($d \approx 16$ mm) while the density value varies from 0.98 to 1.99 g/cm^3. The water absorption values are determined by use of two methods: 24 h of soaking in cold water and 5 h of boiling. The thermal conductivity of unbound, fired LWA particles is determined by measuring the amount of axially transferred heat in the stationary state. The obtained value of the LWA thermal conductivity ($\lambda = 0.0872$ W/mK, $T = 1150$ °C) is suitable for the production of structural concrete blocks with improved thermal insulating properties. Because of their high-porosity and -compressive strength values, the designed LWA could be used instead of the conventional aggregates in the production of concrete blocks. Consequently, a real valorization of the waste material such as fly ash in Serbia was established.

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Introduction

In recent years much effort has been done in order to find the best way to use different kinds of waste materials for the production of the lightweight aggregates (LWA) and lightweight aggregate concrete (LWAC) for the reasons such as: to reduce production costs by replacing natural materials with by-products or to re-use waste materials instead of putting them into the landfill. One of the most used by-products in the production of LWA and LWAC is fly ashes, generated worldwide from thermal coal-fired powers [1]. The current annual production of the coal ash worldwide is estimated around 600 million tones with fly ash about 500 million tones [2]. Although effective measures have been taken in utilizing fly ash by the construction industry in various forms (such as cement replacement or addition in concrete, production of pozzolanic cement [3], brick, and block manufacturing), still a large amount of this material remains unutilized. Converting fly ash into valuable added products, such as LWA and LWAC, offers greater potential for its high-volume utilization and thereby reduces the use of natural weight aggregates.

The applied techniques in manufacturing process of the artificial LWA from fly ashes can be divided in two groups [4]:

- Granulation based on: disk, drum, cone, and mixer
- Compaction: uni-directional piston type compaction, roll pressing, extrusion, and pellet mills.

Based on granulation techniques, the agglomerates are formed without external compacting forces, while in the compaction process the density of the pellets depends upon

the used process. With the compaction technique, the density of the pellets is, in general, higher than that of the pellets produced with the agitation granulation. The quantity of the bonding agent (water) has to be accurately adjusted to avoid squeezing of the pellets. The amount of water is a critical factor because insufficient water quantity produces weak cohesion forces among the particles of the raw material, while large quantity of water influences the creation of the muddy balls instead of the pellets.

Various types of binders (polymeric materials) in recent years are used as sintering aids in the LWA production. Their introduction in fly ash changes the microstructure during the sintering process [5–8]. Some authors observed that the properties of lightweight aggregates depend on the type and amount of the binders which do not alter the chemical composition of the mixture but change the microstructure and the texture proprieties of the aggregate, which influences the thermal properties of the designed LWA [5].

One of the main reasons why LWAs are used instead of the conventional aggregates in the concrete production is their superior thermal insulating properties. Thermal behavior of LWA is related to its thermal conductivity and density values which are influenced by the pore structure. This property depends also on its degree of crystallization. An aggregate with crystalline structure shows higher heat conduction than a vitreous aggregate of the same composition [9]. Waste glass (WG) has been used as additional material which provides sufficient amorphous phase necessary for good thermal insulating properties of the LWA used in the LWAC production. Certain polymers have been used in order to produce appropriate porosity; the pores are formed by gases escaping through the molten material.

The porous LWA acts as an insulating material enhancing the thermal properties of LWAC [10]. The LWA with higher thermal insulating properties (reflected with lower thermal conduction value) possesses lower mechanical properties. Evidently, it is necessary to optimize the LWAs microstructural and textural proprieties in order to obtain products of the requested characteristics.

The objective of this study is to establish the basic understanding of the influence of processing steps in the formation of LWA from fly ash as the main raw material component. Correlations among physical, thermal, and mechanical properties were carried out based on the experimental results.

Experimental

Materials

The LWA aggregates were produced from the mixture of fly ash (FA) obtained from Serbian power plant "Kolubara" and waste glass (WG) from the "Serbian Glass factory", Paraćin, in the presence of carboxyl methyl cellulose (CMC) as a polymer material. The waste glass was used as a component which provides sufficient glass phase during the sintering process, while the polymer material (CMC) was utilized as a plasticizer of the raw material batch and as a pore creator.

The chemical composition of the used components is shown in Table 1, the particle-size distribution (laser diffraction) in Fig. 1 (FA) and Table 2 (sieve analyses of FA and WG) while the morphology, determined based on SEM investigation, in Fig. 2. The thermal behavior of the FA powder is determined based on thermal microscope results, Table 3 and thermal gravimetric analysis (TG), Fig. 3.

Table 1 Chemical composition of the fly ash (FA) and the waste glass (WG) powder (wt%)

Oxides	FA	WG
SiO_2	55.32	72.23
Al_2O_3	25.76	0.61
Fe_2O_3	7.09	1.84
CaO	1.27	6.28
MgO	5.58	4.35
K_2O	1.33	0.36
Na_2O	0.36	11.05
SO_3	1.08	–
Loss of ignition	2.21	–

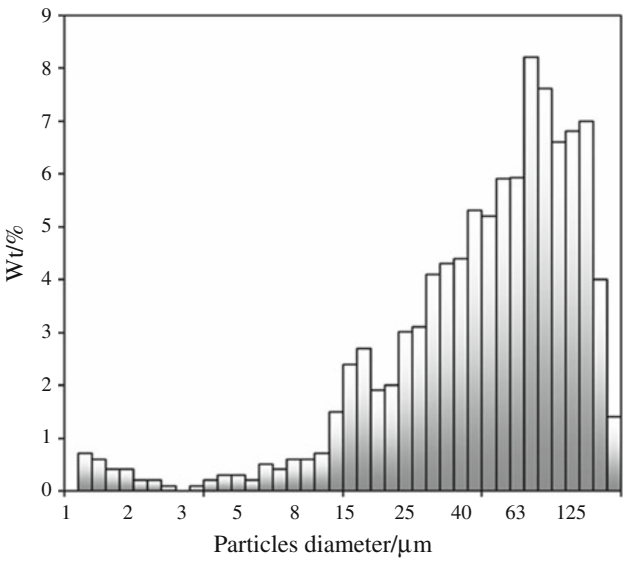

Fig. 1 FA particle-size distribution

Table 2 Sieve analysis of FA and WG powders

Particle size/μm	FA	WG
<63	46	62
63–90	17	18
90–125	13	14
125–250	18	7
25–315	3	–
315–500	1	–
>500	1	–

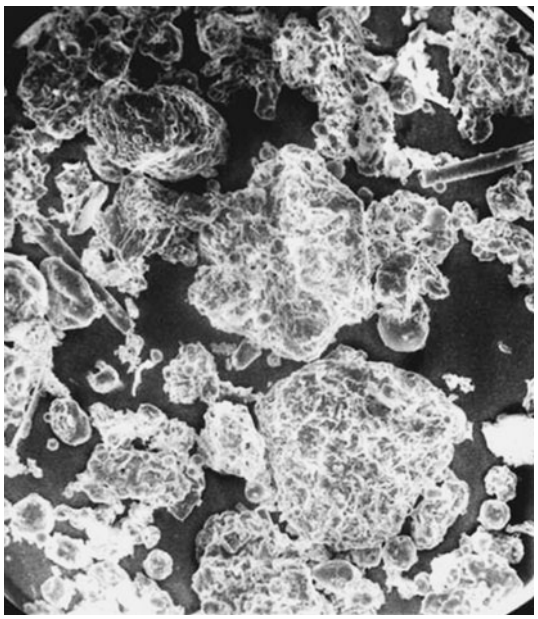

Fig. 2 SEM picture of FA, ×1000

Experimental techniques

Mineral components of the designed mixture:

- Chemical composition of the FA and WG, alkali-silicate chemical analysis,
- Particle-size distribution of the FA was defined by using laser diffraction (Granulometer HR 850) with 30 s ultrasonic mixing before measurement and by sieving analysis (FA and WG).
- Particle morphology of the FA, scanning electron microscopy (SEM) analysis (JEOL, ISM-35).
- Analyses of thermal properties of the FA were carried out based on heating microscope measurements and thermal gravimetric analysis (TG). The changes of the dimensions and shape of the FA tablets (diameter of 3 mm/mass was 5 g) were investigated with a Thermo Microscope "Eras Light" Leitz GMBH D 6330 Wetzlar Type IA (platinum/rhodium/platinum thermocouple, T_{max} = 1600 °C) in the temperature range 20–1400 °C. The thermogravimetric changes were performed using SDT Q600 TG/DSC thermal analyzer (TA Instruments') in the temperature interval from 20 to 1200 °C. The samples in both thermal experiments were heated in air flow with a heating rate of 10 °C/min.

Table 3 Thermal properties of FA powder

Temperature/°C	Property
980	Small dilatation
1034	Beginning of the shrinkage
1168	Significant shrinkage
1269	Softening point
1302	Sphere formation

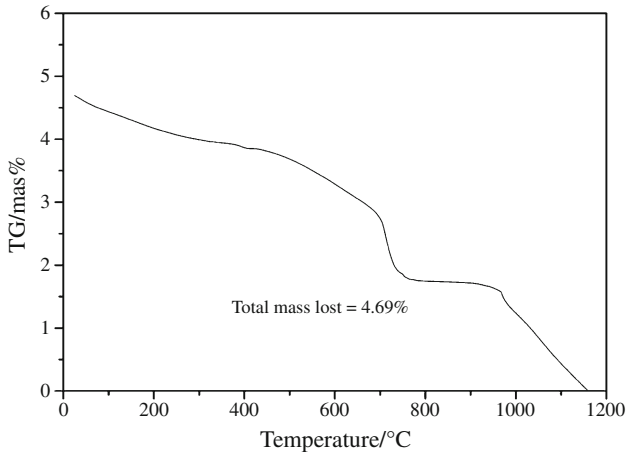

Fig. 3 TG curve of FA sample

LWA particles:

- Water absorption values, (SRPS B.D8.010) 24 h of soaking in cold water and (ASTM C-373/88) 5 h of boiling.
- The apparent and bulk density values, the standard SRPS EN 1097-6 (Annex C),
- Pore-size distribution was analyzed by mercury intrusion porosimetry—MIP (Hg Porosimeter Carlo Erba 2000 WS, Italia), radius range of 0.01–100 μm and by scanning electron microscopy (SEM) analysis (JEOL, ISM-35). The analyzed pellets were not the ones investigated by MIP. The samples after the MIP investigation were crashed and their original porosity was changed.
- Mechanical properties, particle compressive strength [11], five LWA particles of each measurement.
- Thermal conductivity of unbound, fired LWA particles, by measuring the amount of axially transferred heat [12], in the stationary state, through the specimen kept

in the cylindrically shaped container. The bottom of the container was kept at the temperature of the boiling water. The upper side of the measuring container was in contact with another container filled with a known amount of water. When the stationary state was established, before the start of the measuring, the water temperature was registered. After a certain period of time the water temperature measurement was repeated. Knowing the water temperature difference ($t_p - t_0$, $t_p - t_1$), the temperature of the boiling water (t_p), the time of heat transfer (τ), the length (L), and cross-section (S) of the sample container, it was possible to calculate the thermal conductivity (λ) on the basis of the Eq. 1:

$$\lambda = \frac{(mc_v + C_k)L}{S\tau} \ln \frac{t_p - t_0}{t_p - t_1} \quad (1)$$

where mc_v represents the heat capacity of the water located on the top of container and C_k the heat capacity of the calorimetric device.

Procedure

The first stage in the aggregate production was to blend the fly ash (FA) and the waste glass (WG) with a defined quantity of water in the presence of carboxyl methyl cellulose (CMC) as a binder in order to enable the mixture formation for the shaping procedure (extrusion and pelletization). When the most suitable composition was determined, the production of the LWA pellets in an appropriate laboratory line, was started, Fig. 4a. The designed LWA pellets were dried at 105 °C for 8 h in a laboratory dryer and fired in laboratory conditions at three temperatures 1100, 1150, and 1200 °C, with retention at 350 °C, Fig. 4b. It should be noticed that the advantages of this laboratory production line are its continuous production and unimodal spherical green LWA pellets produced with low energy consumption**.** The disadvantage of the described production line is the high amount of water used during the shaping procedure, which implies higher energy consumption during the drying process.

Results and discussion

Based on the results of the chemical composition, Table 1, the FA powder is classified as F class fly ash. The chemical composition of the two components (FA and WG) represents a good source of Al_2O_3 and SiO_2 for the formation of the glassy structure of the future LWA particles during the sintering process. The oxide SO_3 is a potential source of the gas formation, necessary for the porous structure. In order to promote porous structure formation, CMC is added as well. The significant percentage of Na_2O in WG and K_2O in FA presents an important fact for lowering the sintering temperature during the production of the LWA.

Based on the performed laser diffraction, Fig. 1 it could be noticed that FA possesses a high amount of particles within the range of 10–125 μm. The sieve analysis of the FA and WG, Table 2, showed that 46/62 mass% of the FA/WG particles is under 63 μm. In addition, it is possible to observe that FA possesses a significant amount of the particles between 125 and 250 μm.

The results of the heating microscope measurements of the FA powder, Table 3, show that the beginning of the shrinkage occurs at 1034 °C, while the intensive shrinkage temperature is 1168 °C. A wide temperature interval of 101 °C, from 1168 °C (significant shrinkage) to 1269 °C (softening point), could be identified as the fact which presents useful information for setting up an appropriate thermal regime of the designed LWA pellets [13]. The TG results, Fig. 3 show the existence of significant mass loss within 1000–1170 °C. This could be associated with the

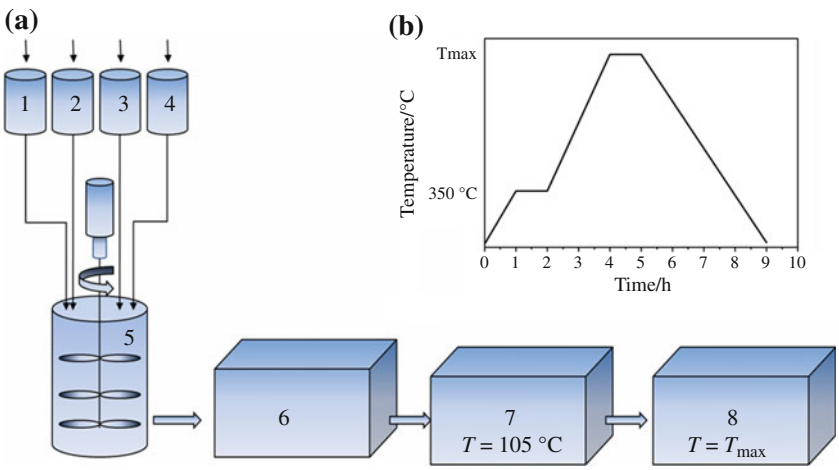

Fig. 4 **a** Laboratory production line for the LWA (*1, 2, 3* raw materials powder silos, *4* water silo, *5* electrical propeller mixer, *6* shaping unit, *7* dryer, *8* electrical furnace) and **b** thermal regime of the LWA pellets

Table 4 Physical and mechanical properties of the fired LWAs

LWA/°C	Water absorption after 24 h/%	Water absorption after 5 h boiling/%	Apparent particle density/kgm^{-3}	Interparticle porosity/%	Thermal conductivity Wm^{-1}K^{-1}	Compressive strength/GPa
$T = 1100$	59.9	68.8	984	47.2	0.0795	0.842
$T = 1150$	42.7	49.8	1226	36.8	0.08720	1.075
$T = 1200$	11.3	14.9	1991	48.3	0.079	1.056

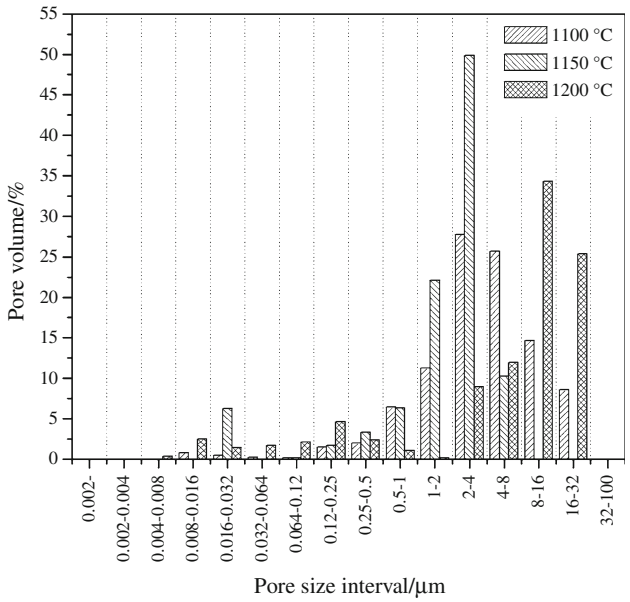

Fig. 5 Pore-size distribution determined by Mercury intrusion porosimetry for LWAs fired at (1100, 1150, and 1200 °C)

intensive shrinkage in the same temperature interval. Based on the SEM results, Fig. 2, a very loose morphology is recognized in the case of the FA particles.

The results of water absorption and apparent particle density, Table 4, and pore-size distribution, Fig. 5, confirm that LWA fired at three temperatures has a complex internal void structure. The apparent particle density values increase along with the firing temperature increase, while the water absorption decreases, Table 4. The apparent particle density and the open porosity value (specified as water absorption) change significantly in a short firing-temperature interval (from 1150 to 1200 °C). The SEM investigations, Fig. 6a–c, point to an increase of glassy phase amount along with the firing temperature increase. The formation of large amount of glassy phase could be identified in the case of the samples fired at 1200 °C, Fig. 6c. This fact affects the increase of the apparent particle density and consequently the decrease of the total porosity.

The pore-size distribution, in Fig. 5, indicates that the dominant pores interval is the function of the firing temperature. For the samples fired at 1100/1200 °C this

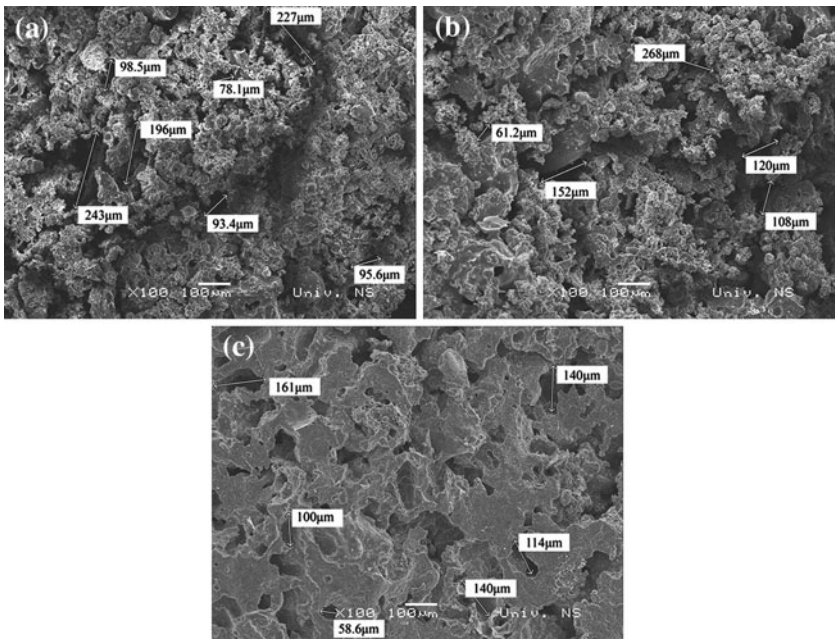

Fig. 6 SEM micrograph (×100) of LWA fired at **a** $T = 1100$ °C, **b** $T = 1150$ °C, **c** $T = 1200$ °C

interval is from 1 to 32 μm/from 2 to 32 μm, while in the case of the samples fired at 1150 °C the dominant pores interval is from 1 to 8 μm. The pores smaller than 1 μm, which presents a real source of water for the internal curing of concrete, are identified in highest percentage (17.8%) in the case of samples fired at 1150 °C. The LWA fired at $T = 1100$ °C has 11.7% of the pores of this diameter, while LWA fired at $T = 1200$ °C has 16.2%. The SEM micrographs of these samples, Fig. 6a–c, indicate the presence of larger pores (up to 270 μm) than in the case of the Mercury intrusion porosimetry. The discrepancy between the results of these two methods originates from the limitations of the MIP method. The larger pores are partially excluded in the case of this method, due to withdrawal of mercury as their capillary pressure is lowered [14]. The two methods have to be taken as complementary in the case of these systems of complex textural proprieties with a serious content of larger pores (identified based on SEM investigation). As the larger pores of the LWA pellets have a decisive role considering thermal conductivity, their correct identification is a very fact [15].

The differences in the values of thermal conductivity, Table 4, are discussed with respect to the influence of the quantity of glassy phase, apparent particle density, and interparticle porosity. The increase of the amount of glassy phase together with the decrease of apparent particle density (followed by the increase of porosity) decreases the thermal conductivity of the LWA particles. The interparticle porosity is also present due to the fact that it is not possible to pack the LWA particles in the experimental container without void spaces. The value and shape of the void spaces depend on shape of the particles. The diameter of the interparticle voids of the LWA particles ($d = 16$ mm) is higher than 1 mm, the value which enables good preconditions for the convective heat transfer. Therefore, the influence of the interparticle porosity on thermal conductivity value is lower in comparison to the influence of the porosity of LWA particles.

The relative influence of the glassy phase, apparent particle density, and interparticle porosity on the thermal conductivity is shown in Table 5. Numbers 1, 2, and 3, in this table, present the hierarchy influence of the defined parameters. In the case of the samples fired at 1100 °C, the value of the apparent particle density has the maximal influence on the thermal conductivity, while for the samples fired at 1200 °C, the prime control parameters are the amount of the glassy phase and the interparticle porosity value [16]. Considering the influence of the above specified parameters (glassy phase, apparent particle density, and interparticle porosity) on the value of thermal conductivity of the samples fired at 1150 °C, it can be specified as average. In addition, the value of the thermal conductivity of these samples is under the influence of the presence of crystalline phase. This fact is documented by the highest mechanical characteristics of these samples Table 4.

Table 5 Relative influence of the amount of glass phase, apparent particle density, and interparticle porosity on the decrease of thermal conductivity value

LWA/°C	Amount of glassy phase	Apparent particle density	Interparticle porosity/%
$T = 1100$	3	1	2
$T = 1150$	2	2	3
$T = 1200$	1	3	1

Conclusions

The lightweight aggregate based on fly ash was obtained in the continuous production line using specific granulation process (extrusion and pelletization). The LWA pellets were fired at three different temperatures (1100, 1150, 1200 °C) and uni-modal particles ($d = 16$ mm) were produced. After a detailed analysis of the characteristics of the particles, the lightweight aggregates fired at 1150 °C were selected for the production of the lightweight concrete on the basis of the following: the highest amount of pores less than 1 μm, the lowest value of interparticle porosity, good mechanical properties, and satisfactory value of thermal conductivity ($\lambda = 0.0872$ W/mK). The aggregates of the above characteristics can provide good thermal properties of the structural concrete blocks.

References

1. Yao Y, Yang DW, Zeng JL, Sun LX, Li WJ. Influences of fly ash and fluorgypsum on the hydration heat and compressive strength of cement. J Therm Anal Calorim. 2011;106:869–74.
2. Joshi C, Lothia RP. Fly ash in concrete: production, properties and uses. Advances in concrete technology. New York: Gordon and Breach Science Publishers; 1997.
3. Nochaiya T, Wongkeo W, Pimraksa K, Chaipanich A. Microstructural, physical, and thermal analyses of Portland cement–fly ash–calcium hydroxide blended pastes. J Therm Anal Calorim. 2010;100:101–8.
4. Bijen JMJM. Manufacturing processes of artificial lightweight aggregates from fly ash. Int J Cem Compos Lightweight Concr. 1986;8(3):191–9.
5. Ramamurthy K, Harikrishnan KI. Influence of binders on properties of sintered fly ash aggregate. Cem Concr Compos. 2006;28:33–8.
6. Verma CL, Handa SK, Jain SK, Yadav RK. Techno-commercial perspective study for sintered fly ash lightweight aggregates in India. Constr Build Mater. 1998;12:341–6.
7. Yang CC, Haung R. Approximate strength of lightweight aggregate using micromechanics method. Adv Cem Based Mater. 1998;7:133–8.

8. Majchhrzak-Kuceba I. Thermogravimetry applied to characterization of fly ash-based MCM-41 mesoporous materials. J Therm Anal Calorim. 2011. doi:10.1007/s1097301119088.
9. Neville AM. Properties of concrete. 4th ed. Harlow: Longman; 1995.
10. El-Gamal SMA, Hashem FS, Amin MS. Thermal resistance of hardened cement pastes containing vermiculite and expanded vermiculite. J Therm Anal Calorim. 2011. doi:10.1007/s10973 01116809.
11. Li Y, Wu D, Zhang J, Chang L, Wu D, Fang Z, Shi Y. Measurement and statistics of single pellet mechanical strength of differently shaped catalysts. Powder Technol. 2000;113:176–84.
12. Hamdhan IN, Clarke BG. Determination of thermal conductivity of coarse and fine sand soils. In: Proceedings of World Geothermal Congress 2010, Bali, April 2010.
13. Komljenović M, Petrašinović-Stojkanović Lj, Baščarević Z, Jovanović N, Rosić A. Fly ash as the potetntional raw mixture component for Portland cement clinker synthesis. J Therm Anal Calorim. 2009;96:363–8.
14. Wardlaw NC, McKellar M, Yu L. Pore and throat size distributions determined by mercury porosimetry and direct observation. Carbonate Evaporites. 1988;3:1–15.
15. Kamseu E, Ceron B, Tobias H, Leonelli E, Bignozzi MC, Muscio A, Libbra A. Insulating behavior of metakaolin-based geopolymer materials assess with heat flux mater and laser flash techniques. J Therm Anal Calorim. 2011. doi:10.1007/s1097301 117989.
16. Rice RW. Porosity of ceramics. Marcel Dekker Inc., Berlin; 1998.