

Valorization of lignite combustion residues and ferroalumina in the production of aggregates

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ABSTRACT

The present research study investigates the synergy of industrial solid by-products from lignite combustion (fly ash and bottom ash) and aluminum production (ferroalumina) in the production of lightweight aggregates (LWA). The process consists of two stages, pelletization and sintering. Bottom ash (BA) is used as the principal raw material in mixtures while ferroalumina (FAL) is added in lower percentages (5–30 wt%). BA carbon content is used as the fuel of sintering process in high temperatures, around 1250 °C, and gas generation is responsible for porous structure formation. Physical properties such as porosity, water absorption and bulk density, of sintering products are measured. Increase of FAL percentage in sintering mixtures results in decrease of porosity from 61% to 35% and of water absorption from 61% to 21% and in increase of bulk density from 1.02 g/cm³ to 1.80 g/cm³ of the produced aggregates. Aggregates produced by FAL addition up to 20 wt% are characterized as LWA. Aggregates formed are used in the production of concrete specimens. Compressive strength of concrete increases by increasing FAL addition in aggregates from 5 wt% to 15 wt% (highest strength value), while decrease by increasing FAL addition from 20 wt% to 30 wt%. FAL addition in lignite ashes sintering mixtures (up to 15 wt%) is considered as an important parameter for enhancing aggregates strength.

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1. Introduction

A large part of Greece's energy demand is covered by lignite combustion in West Macedonia and Peloponnesus. This energy is produced exclusively in PPC's (Public Power Corporation) plants and results in the production of over 14 Mt/y solid by-products. Fly ash (FA) holds the 75% of the total production while bottom ash (BA) the rest. 4 Mt/y of these by-products are produced at PPC plants in Megalopolis field (Peloponnesus). Since 1982, the 12%, approximately [1], of the production of Megalopolis FA is utilized in the production of Portland cement the so-called Greek type FA-cement. In parallel FA from Ptolemais plants (Macedonia) has already been used in large construction projects such as the Platanovrisis Dam at Nestos. Lignite BA is not utilized in cement production, mainly due to high percentage of carbon contained. As a result, research effort is put on the development of processes capable of utilizing the above by-product (BA) especially directed to massive applications. Such a proposed process is the production of lightweight aggregates (LWA) by grate sintering of BA and FA mixtures for use in structural and insulating lightweight aggregate concrete [2]. Sintering of BA and FA pellets, around 1250 °C, resulted in the production

of low density (0.83–0.91 g/cm³) LWA, which conform to ASTM standards specifications for production of structural and insulating lightweight aggregate concrete. Rapid (grate) sintering is recommended for LWA formation instead of slow sintering [3,4], as it avoids total densification and, thus, allows formation of porous structure inside the pellet [5].

The successful experimental results of valorization of lignite combustion solid residues in the production of LWA offer new research opportunities for valorization of solid by-products from different industrial processes. Such a by-product, produced in large quantities in Greece (700 Mt/y), is ferroalumina (FAL). FAL is the main solid by-product of the production of aluminum by the digestion of bauxite ores with caustic soda, according to Bayer process. Its chemical composition consists of six major constituents, namely Fe₂O₃, Al₂O₃, CaO, SiO₂, TiO₂ and Na₂O, while Fe₂O₃ and Al₂O₃ are the most abundant ones. Research efforts are put on the valorization of FAL (produced in Greece) as raw material (up to 5 wt%) in cement production [6]. Successful research has also been performed for valorization of FAL as raw material in ceramic production [7], bricks and roofing tiles. Another possible application for FAL valorization is the production of aggregates.

Research works have been performed concerning the production of synthetic aggregates using FAL as raw material. Bayer [8] reports the production of lightweight porous aggregate using FAL as the principal raw material, but without any details of the pro-

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cess involved. Wargalla [9] presents the production of LWA of bulk density 700 kg/m^3 as a result of firing 1:1 mixture of FAL and FA. Blank [10] performed experiments on bloating of pellets consisting of FAL alone and, also, in collaboration with numerous substances (up to 10 wt%), such as carbonaceous and waste materials as well as common chemicals. Firing of FAL alone, around 1260°C , resulted in the formation of strong heavyweight aggregates, while LWA could not be formed by any of the added materials. The failure of producing LWA by using FAL as the principal raw material (90–100 wt% in mixture) is explained by its high melting point (1316°C), its narrow softening range around this temperature and its high specific gravity (because of high percentage of iron oxide).

The present study attempts to investigate the collaboration of FAL, in low percentages, with Megalopolis lignite ashes, as the principal raw materials, in the production of LWA by a two step process, pelletizing and sintering [2]. Concrete specimens were produced using the sintering products and their compressive strength was measured.

For the sintering process carbon content of BA is utilized as a fuel. Mixtures of constant BA percentage (constant fuel percentage) and altering percentages of FAL and FA are prepared. FAL percentage was altered from 5 wt% to 30 wt% in purpose of examining the interaction between these two different by-products (lignite ash and FAL) during sintering. Small amount (3 wt%) of metallurgical lime is used to facilitate the formation of the pellets. For pelletization process the water content of BA, usually in the range of 30–40%, is used, with minor addition.

2. Materials and methods

2.1. Characterization of raw materials and sintering mixtures

The raw materials used for the experiments are lignite FA, BA and FAL. Metallurgical lime is used, as well. Chemical composition of raw materials is presented in Table 1. FA and BA are classified as type F ashes according to ASTM C 618 specifications [11], due to high total percentages of SiO_2 , Al_2O_3 and Fe_2O_3 (higher than 70 wt%). The main difference between the two ashes is the high carbon content of BA (10.14 wt%) compared to that of FA (1.31 wt%). FAL is characterized by high percentage of Fe_2O_3 (41.7 wt%) and Al_2O_3 (18.01 wt%). Metallurgical lime is used as a binder to assist the formation of pellets. The mixtures prepared and the proportions of raw materials used are presented in Table 2.

Sintering of Megalopolis lignite ashes requires carbon content higher than 6 wt% [2]. As a result, BA percentage in all mixtures is adjusted to 60 wt%. In order to examine the interaction between FAL and lignite ashes during sintering, FAL percentage is increased from 5 wt% to 30 wt% from mixture M1 to M6. Conversely, FA percentage is decreased from 32 wt% to 7 wt%, as a result of FAL increase.

In Fig. 1 the cumulative curves for the particle size distribution of BA, FA and FAL are depicted. FA and FAL are characterized fine grained materials, as 82% and 96% of particles diameter respectively, is less than $100 \mu\text{m}$. BA is coarser with maximum diameter of agglomerates $4000 \mu\text{m}$ and only 20% of particles size is less than $100 \mu\text{m}$. Typical diffraction patterns for BA and FA are presented in Fig. 2. The reflection peaks of quartz (SiO_2), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and gelhenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) are identified in both FA and BA. The

Table 2
Sintering mixtures composition.

Mixture symbol	BA (wt%)	BR (wt%)	FA (wt%)	Metallurgical lime (wt%)
M1	60	5	32	3
M2	60	10	27	3
M3	60	15	22	3
M4	60	20	17	3
M5	60	25	12	3
M6	60	30	7	3

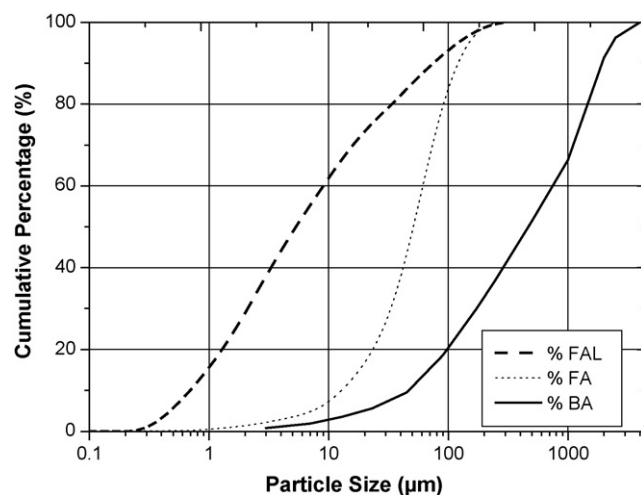


Fig. 1. Particle size analysis of BA, FA and FAL.

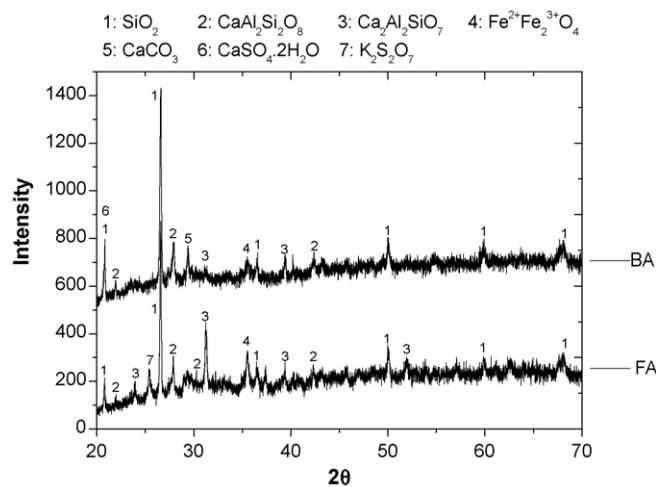


Fig. 2. XRD patterns of BA and FA.

peak at about $37^\circ-2\theta$ is attributed to magnetite, $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$. The magnetic properties of the powders were verified by the attraction of the BA and FA particles by an alnico magnet. Calcite (CaCO_3) is identified only in BA. Typical diffraction patterns for FAL are presented in Fig. 3. Hematite is the major peak identified.

Table 1
Chemical composition of raw materials.

wt%	Al_2O_3	CaO	SiO_2	Fe_2O_3	TiO_2	Na_2O	K_2O	MgO	SO_3	C	Total
FA	22.65	8.85	49.4	7.42	0	0.85	1.39	1.62	2.55	1.31	96.04
BA	19.93	7.51	44.6	6.28	0	0.75	1.22	1.43	2.24	10.14	94.1
RM	18.01	14.13	7.58	41.7	4.16	5.11	0.76	0.19	0	0	91.64

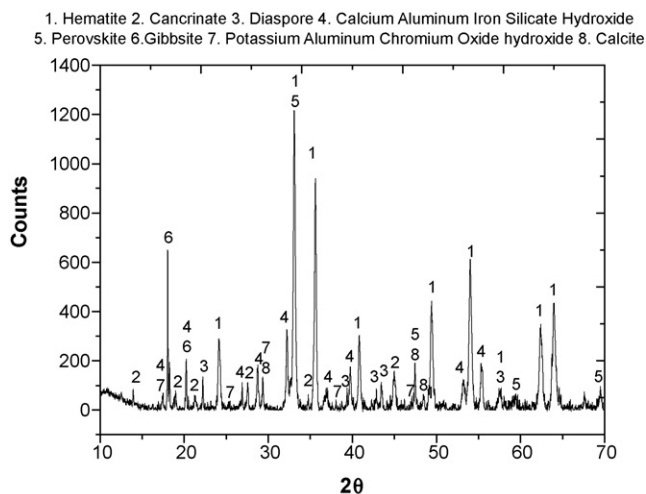


Fig. 3. XRD patterns of FAL.

2.2. Experimental

The developed process for the production of LWA from lignite ashes (BA and FA) and FAL consists of two stages, pelletization and sintering respectively.

Prior pelletization, BA, FA and FAL dusts are thorough mixed in pots with addition of 3 wt% fine grained metallurgical lime as binder. Subsequently, 3–10 mm in diameter pellets are formed by means of a pelletizing disc rotating at 12–15 rpm at a slope of 45° [12,13]. Minor water addition is required for the formation of the pellets due to the relatively high water content of BA, which is usually in the range of 30–40%.

For the sintering process, the pellets are loaded in a sinterpot of 0.04 m² surface so to form a 0.20–0.25 m height air permeable bed. The process is started with the ignition of a charcoal layer placed at the surface of the bed. Air is drawn downwards through the grate, by means of an exhaust blower connected from underneath to the grate. In this way, suction pressure is created through the bed. The suction pressure was adjusted to 10–15 bar. The narrow combustion zone developed initially at the top layer travels through the bed raising the temperature of the bed layer by layer, to the sintering level. In the combustion zone, bonding takes place between the grains and a strong and porous aggregate is formed. The process is over when the combustion zone reaches the lowest layer of the bed [14,15].

The experimental installation with the pelletizing disc and sinter pot devices is schematically presented in Fig. 4. In Fig. 5, view of part of the opened pot with the sinter cake in it is depicted.

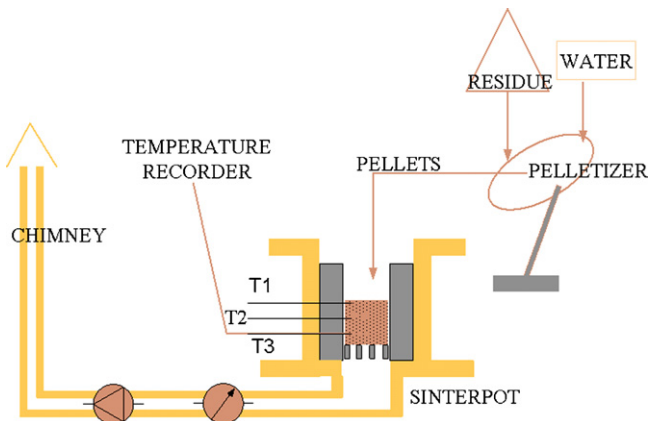


Fig. 4. Schematic diagram of the sintering installation.



Fig. 5. View of the opened sinterpot with the formed sinter cake inside.

3. Results and discussion

3.1. Sintering products

All mixtures presented in Table 2 are sintered in the sinterpot. The sintering process is performed successfully and a hardened porous cake is formed for each mixture. Sintering is carried out by high temperatures around 1250 °C.

Chemical composition of the produced sinters is presented in Table 3. Gradual substitution of FA by FAL in mixtures M1–M6 resulted in reduction of SiO₂ from 47.50 wt% (M1) to 35.71 wt% (M6) and, conversely, increase of Fe₂O₃ from 9.19 wt% (M1) to 18.51 wt% (M6). Slight (~2 wt%) increase of CaO percentage and decrease of Al₂O₃ percentage is also observed. Carbon (C) and sulphur (S) percentages are expected to be less than 1% as a result of high temperature rise during sintering.

The results of XRD analysis for all sintered products are presented in Fig. 6. Sintered mixtures M1–M3 show similar crystalline structure. Intensity of quartz (SiO₂) peaks is decreased and intensity of anorthite (CaAl₂Si₂O₈) peaks is increased, compared with BA and FA XRD patterns. Furthermore, hendebergite (CaFeSi₂O₆) and magnetite (Fe₃O₄) peaks are identified. Increase in magnetite content is the result of the localized carbothermic reduction of hematite (Fe₂O₃). Intensity of quartz, anorthite and hendebergite is gradually decreased from mixture M4 to M6, while intensity of gelhenite (Ca₂Al₂SiO₇) is increased. Gelhenite is the main crystalline peak in mixture M6.

In purpose of better understanding of mechanisms occurring during sintering, BA samples are heated in different temperatures from 110 °C to 1100 °C and analyzed by XRD method. The results are presented in Fig. 7. Anorthite (secondary) is formed over 900 °C and hendebergite over 800 °C. Calcite is decomposed over 600 °C and gelhenite (Ca₂Al₂SiO₇, secondary) is formed over 900 °C. Gelhenite formation is probably caused by CaO released from cal-

Table 3
Chemical composition of produced sinters.

Oxides	M1 (wt%)	M2 (wt%)	M3 (wt%)	M4 (wt%)	M5 (wt%)	M6 (wt%)
SiO ₂	47.5	45.14	42.78	40.41	38.06	35.71
Al ₂ O ₃	22.29	22.00	21.72	21.44	21.15	20.87
Fe ₂ O ₃	9.19	11.06	12.94	14.80	16.65	18.51
CaO	11.86	12.14	12.41	12.69	12.95	13.22
MgO	1.63	1.54	1.46	1.39	1.31	1.23
Na ₂ O	1.09	1.31	1.54	1.78	2.01	2.24
K ₂ O	1.35	1.30	1.27	1.23	1.20	1.16
TiO ₂	0.23	0.46	0.68	0.91	1.14	1.37
Total	95.14	94.95	94.80	94.64	94.46	94.30

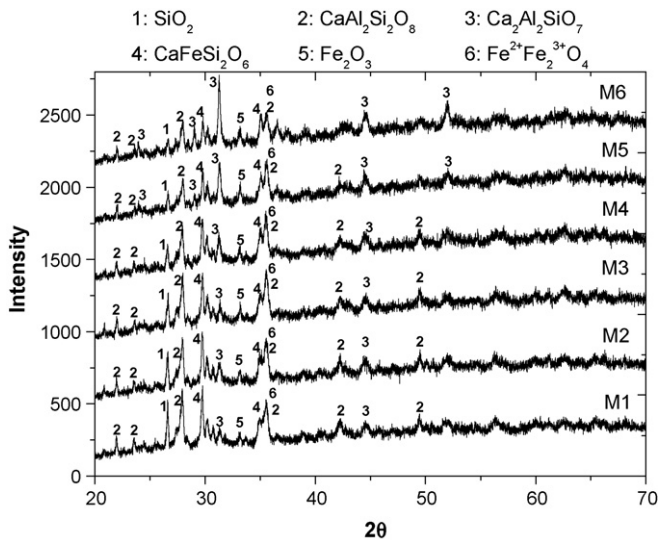


Fig. 6. XRD patterns of the sintered products.

cite decomposition. Intension of gelhenite peaks is decreased over 1000 °C.

Optical observation by means of a stereoscope of sintered pellets is presented in Fig. 8, which shows the formation of glassy phase on the outer surface of the sintered pellet. The glassy phase inhibits produced gases to escape from the pellet to the outside environment, and porous structure is formed inside the pellet.

Porosity, water absorption, bulk density and unit weight are measured for all mixtures aggregates. For this purpose, sintered cake is mechanically crushed into aggregates with a size from 8 mm to 16 mm. The measurement of porosity, bulk density and water absorption of sintered pellets are performed according to ASTM C373–88 specifications [16]. Porosity values vary from 35% to 60% and water absorption values range from 21% to 61% (Fig. 9). Increase of FAL in sintering mixtures results in decrease of porosity and water absorption and increases the bulk density. Decrease of porosity and water absorption can be attributed to the lower expansion that occurs during sintering with higher FAL additions. Increase of FAL addition causes variations in the amounts of the fluxing agents in the mixture. More specifically SiO_2 content decreases as Na_2O and CaO ones increase respectively. This affects the amount of liquid phase formed as well as its viscosity. These are of the main parameters that influence the bloating of the pellets. Increase of



Fig. 8. Glassy phase formation on the outer surface of sintered pellet.

bulk density can be explained by lower expansion and increase of specific gravity of raw materials. Specific gravity of hematite is higher than the ones of the rest constituents of the raw mixture [10].

For the unit weight measurements, the sintered pellets are mechanically crushed in fine aggregates (0–5 mm) for all mixtures' aggregates. The measurements are performed according to ASTM C29 [17] and the results are shown in Fig. 10 together with the bulk density ones. Increase of FAL addition result in increase of unit weight of sintered products from 925 kg/m³ to 1175 kg/m³ as bulk density increases from 1.02 g/cm³ to 1.8 g/m³. According to ASTM C330 specifications [18] the maximum unit weight of fine (<9.5 mm diameter) aggregates is 1120 kg/m³. As a result, aggregates produced from sintering of mixtures M1–M4 (5–20 wt% FAL) can be characterized as lightweight aggregates, while aggregates from mixture M5 (25 wt% FAL) are close to the upper limit of acceptable unit weight for LWA. Aggregates from mixture M6 cannot be characterized as lightweight ones.

3.2. Mechanical properties of synthetic aggregate concrete

Concrete specimens with aggregates of all sintered mixtures are prepared for compressive strength tests. Preparation and strength tests are performed according to EN196-1 specifications [19]. Specimens of 0.16 m × 0.04 m × 0.04 m dimensions are used for the tests. In Table 4 the amounts of the materials used for the preparation

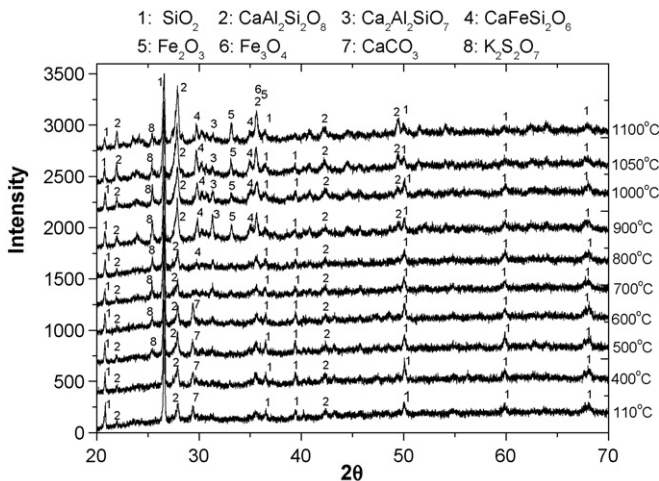


Fig. 7. XRD patterns for BA samples heated from 110 °C to 1100 °C.

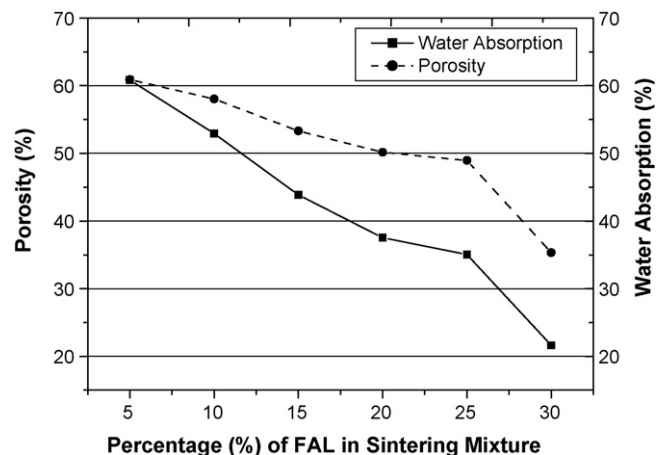


Fig. 9. Porosity and water absorption of the produced aggregates.

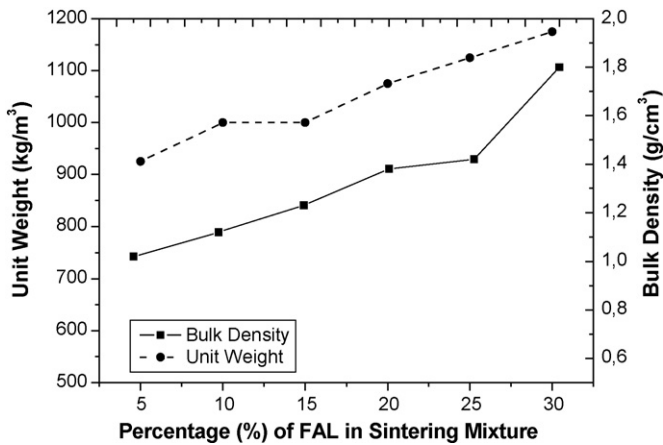


Fig. 10. Unit weight and bulk density of the produced aggregates.

Table 4

Composition of concrete specimen produced with M1–M6 aggregates.

Raw materials	Weight (g)						
	S _{M1}	S _{M2}	S _{M3}	S _{M4}	S _{M5}	S _{M6}	S _{ref}
Aggregates	780	844	844	907	949	991	1350
Cement	450	450	450	450	450	450	450
Water	315	315	315	315	315	315	225

of the three specimen required for the 2, 7 and 28 days compressive tests is presented for the M1–M6 mixtures denoted as S_{M1}–S_{M6} respectively. The amounts required for the preparation of three standard concrete specimens S_{ref} is also presented. A significant reduction in weight is observed if S_{ref} is compared to the lightweight concrete specimens S_{M1}–S_{M6} respectively. Moreover an increase of the weight with increasing in FAL addition from S_{M1} to S_{M6} is also observed.

The compressive strength tests were performed for 2, 7 and 28 days curing period at 20 °C and 95% humidity conditions. The results are depicted in Fig. 11. Specimens with aggregates M2–M4 (10–20 wt% FAL in mixture) show the highest strength values, between 38 MPa and 39 MPa at 28 days curing period. The strengths that have been reported in the literature for 28 days curing period varies from 25.4 MPa to 46.4 MPa for lightweight concretes with densities 1360 kg/m³ and 2335 kg/m³ respectively [20]. In comparison to the normal weight concrete, the speci-

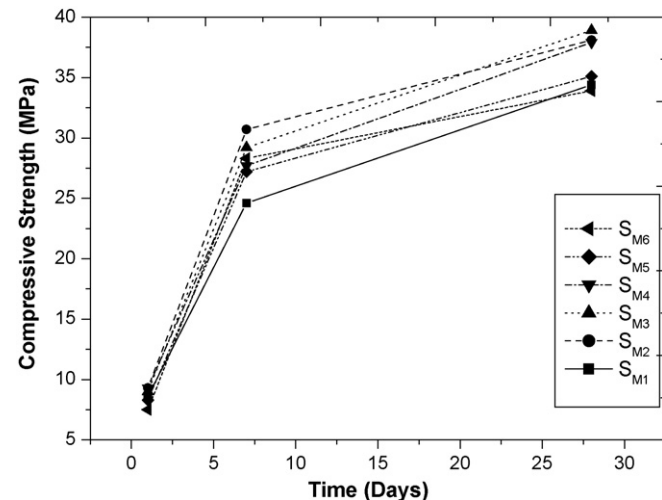


Fig. 11. Development of compressive strength for 2, 7 and 28 days curing period.

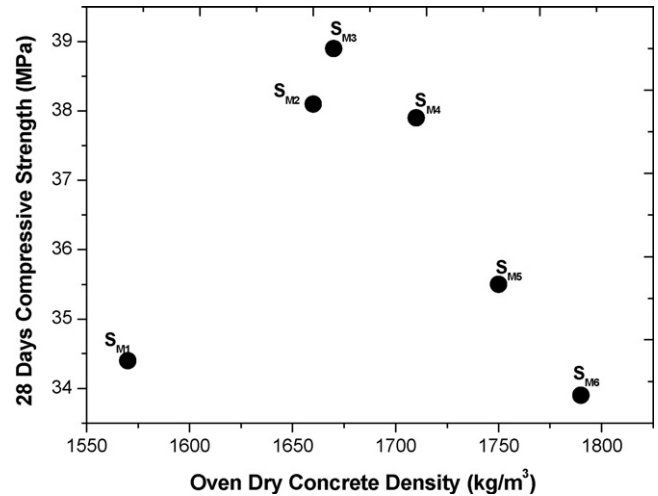


Fig. 12. Compressive strength and oven dry density of concrete specimens.

mens S_{ref} presented 15 MPa, 27 MPa and 43 MPa for 2, 7 and 28 days curing period respectively. Fig. 12 presents the results of compressive strength and oven dry density of concrete specimens at 28 days. Concrete density increases from 1570 kg/m³ to 1790 kg/m³ with increase in FAL addition from 5 wt% to 30 wt%. Compressive strength increases from 34.4 MPa to 38.9 MPa for the specimen M1–M3 which corresponds to an increase in FAL addition from 5 wt% to 15 wt% respectively. The later specimen M3 exhibits the maximum strength value. Further increase in FAL addition, specimens M4–M6, increases concrete density and decreases compressive strength.

According to the XRD analysis (Fig. 6) of the produced aggregates, their crystallization influences the strength of the concrete (Fig. 12). In the XRD patterns of M2, M3 and M4 mixtures a hump characteristic of the formation of amorphous phase is observed in the range from 20°–2θ to 35°–2θ, which in the case of M3 is more intent. An important parameter that seems to affect the strength of aggregates and concrete is the increase of the magnetite (Fe²⁺Fe₂³⁺O₄). If Fe²⁺ is available then it acts as a flux during sintering and lowers the melting point of mixture. Increase of FAL results to increase of Fe₂O₃ composition in mixture and, in turn, increase of quantity of Fe²⁺ formed. Increase of Fe²⁺ enhances crystallization of new mineral phases (anorthite, hendebergite), which are responsible for increase in aggregates strength, up to 15 wt% FAL (M3). Further increase of Fe₂O₃ (M4–M6) is accompanied by significant decrease of SiO₂ composition in mixture. As a result, there is not enough SiO₂ available for crystallization of new (rich in Si) compounds like anorthite and hendebergite and strength of aggregates decreases.

4. Conclusions

In purpose of developing new methods for valorization of FAL, sintering tests are performed with mixtures of lignite ashes and FAL for the production of aggregates and concrete. BA is used as the principal raw material (60 wt%), while FAL is added in lower percentages from 5 wt% to 30 wt%. Increase in FAL addition in sintering mixture results in increase of the unit weight and density of the produced aggregates. Porosity and water absorption values of aggregates vary between 35–61% and 21–61% respectively, and bulk density values vary between 1.02 g/cm³ and 1.80 g/cm³. Aggregates produced with FAL addition up to 20 wt% are characterized as lightweight ones, according to ASTM 330 specifications. The produced aggregates are used for concrete production. The compressive strength measurements show that addition of FAL

up to 15 wt% in sintering mixtures enhances strength of produced concrete. Addition of FAL between 20 wt% and 30 wt% results in decrease of concrete strength, as well as, in further increase of the concrete density. FAL in combination with BA and FA, can be considered as a potential raw material, for the production of LWA by means of the proposed sintering process.

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