Evaluating the properties and mineral phases of the expanded clay aggregates with the bentonite additive material

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Abstract. Additive materials are the perfect solutions to improve the physical, mechanical and expansion properties of lightweight expanded clay aggregates (LECA). This work focused on studying the effect of bentonite materials on physical, mechanical, expansion properties and mineral phases of expanded clay aggregates. Samples were collected from Mályi quarry Miskolc, Hungary. These samples were studied by XRF, XRD, SEM and heating microscope. In addition, the physical and mechanical properties of specimens were measured according to relating standards. Results showed that, addition of bentonite material to the clay samples has great effect on bulk density, sintering and melting point and compressive strength of the aggregates. By using the three different amounts (5 %, 10 % and 20 %) of bentonite with the LECA, compressive strength of the aggregates was enhanced by 48 % to 112 % compared to aggregates without bentonite. 10 % of bentonite with aggregates was enhanced the height expansion of the aggregates by 50–68 %. In addition, 10 % of bentonite with LECA was most crucial, which decreased bulk density of aggregates by 5 % to 20 % compared with other added amounts of bentonite. According to XRD analysis, hercynite was one of the phases, which can control compressive strength of aggregates.

Keywords: Bentonite, Lightweight, Aggregates, Phases

1. Introduction
Lightweight aggregates (LWA) are one of the most crucial materials, which are used in the construction and building materials. Lightweight aggregates become the centre of attention of the whole world, because these types of aggregates have the perfect properties of good thermal behaviour, acoustic insulation and good fire resistance. Controlling the production of lightweight aggregates, most important factors are expanding, physical and mechanical properties. Mechanism of expansion in lightweight aggregates can be achieve in several steps. First step is the development of gases at a specific temperature, where material is in its visco-plastic state. During the second step, gases were trapped by partly molten state. Finally, after cooling, the molten phases are remained as a glassy phase, which include of different crystalline compounds depending on the composition of the material [1]. If the temperature is extremely high during sintering, excess gas may be generated, increasing the total porosity and producing continuous pores [2]. In addition, further increases in temperature above the pyro-plastic range can result in viscous flow, reducing porosity and pore size [3]. Change in mineral phase in products has an significant effect on physical and mechanical properties of LWA, e.g. more mullite mineral enhanced the compressive strength of the aggregates after firing [4]. Additive materials seems to be perfect solutions to improve physical, mechanical and expansion properties of lightweight
expanded clay aggregates [5, 6]. In earlier studies different types of additive materials were used. Some of these additives can enhance the expansion, e.g. Fe metal, but on the other side, bulk density and compressive strength decreased [7]. Others like CaF$_2$ increased glassy phases in LWA and decreased sintering and melting temperature approximately 125$^\circ$C to 200$^\circ$C lower than temperature used by the LWA manufacturing sector [8,9]. Whilst with the addition of carbon fiber particle density decreased, total porosity and compressive strength increased [10]. However there are some materials which is expandable such as bentonite. It is a clay soil with significant engineering claims, especially in the construction of municipal and barriers for the storage of spent nuclear fuel [11, 12, 13, 14, 15, 16]. Bentonite formed by weathering effect on volcanic ash, mainly consists of montmorillonite with different composition of other minerals, such as quartz, sodium, and calcium feldspar [17]. Physical and chemical properties of clay typically depend on composition, structure, particle size, surface area, ion exchange capacity, adsorption, and swelling capacity [18]. Generally, bentonite is categorized into two different types, such as Na-bentonite which is considered as high swelling clay, while Ca-bentonite has less swelling capacity upon hydration with water [19]. Structurally, montmorillonite is classified as 2:1 layered aluminosilicate, and it consists ideally of one alumina octahedral sheet between two silica tetrahedral sheets [20, 21, 22, 23]. In construction and building material application, the effect of calcined bentonite on the fresh and hardened properties of mortar and concrete were studied by some researches. Results showed that with increasing amount of bentonite the workability, fresh density and water absorption of concrete decreased while compressive strength increased. [24,25]. Researchers [26] mentioned a positive influence of calcined bentonite when it was used as a substituting material for cement. Calcined bentonite had effect on the pozzolanic activity, consistency and setting time, when it was added to cement paste [27]. Others [20] analyzed strength activity index of the cement with bentonite in its natural state and after heating at (500- 900)$^\circ$C and it was pointed out that the strength activity index met the requirements at 28 days curing. In this study the effect of bentonite as additive materials were examined on expansion, density and compressive strength of lightweight expanded clay aggregates and change in mineral phases were also identified and analyzed.

2. Material and methods

Three types of clay samples were collected from Mályi quarry, Miskolc, Hungary. Clays were named as follows: grey clay: G, blue clay: B and yellow clay: Y. Samples were dried at 105$^\circ$C for 24 h in an air circulating electric furnace. They were ground for a few seconds to decrease the particle agglomeration and milled to pass through a No. 100 mesh (150 $\mu$m) for further measuring. Chemical composition of the samples was studied by using an X-ray fluorescence spectrometer, in addition the results of the chemical composition after calcined basis were plotted in the Riley diagram [28]. Mineral phases were analysed using X-ray diffraction (Rigaku Miniflex II, Cu Kα, 2θ range from 3° to 90°) and for interpretation the raw data using the software X’Pert HighScore plus. The expansion of clay samples was measured by heating microscope (Camar Elettronica). The clays were mixed together with 5 %, 10 % and 20 % of bentonite materials. Green pellets (five each) were produced by hand-rolling. Pellets were dried at 105 $^\circ$C in a drying chamber. Then, dried pellets were sintered at three different temperatures. Temperature values were set to 1175$^\circ$C, 1200$^\circ$C, and 1225$^\circ$C respectively, with 10 minutes of residence time at maximum temperature. Lastly, after the heating process at 1175$^\circ$C – 1225$^\circ$C, sintered products were naturally cooled down in the furnace, and their physical and mechanical properties were studied. Uniaxial compressive strength and bulk density were measured according to UNE-EN-13055-1 European standards. Bulk density was measured using the Archimedes method after the LECAs were placed in water for 24 h [29]. Compressive strength was measured by an INSTRON universal tester with a cross-head speed of 0.1 mm/s. Compressive strength of the LECA was calculated by [30]. Microstructure of LECAs was observed with an environmental scanning electron microscope (ESEM) with EDAX under high vacuum mode (Carl Zeiss EVO MA10).
3. Results

3.1. Effect of bentonite on clay expansion

According to Riley theory (1951), chemical composition (SiO₂, Al₂O₃ and total flux) of the expanded clay samples is the most critical key to define expanded zone for the samples. For clay we used in this experiment, the ranges of these oxides were: SiO₂ range (62.23 % - 64.97 %), followed by Al₂O₃ range (17.31 % - 17.94 %) and total flux range (17.43 % - 19.31 %). Illustrating these values in Fig. 1a., it can be seen that the five samples located in bloating area so theoretically these samples can obtain a convenient viscosity to trap a significant amount of the gaseous components, resulting in the formation of expanded structure of LECA [4, 31]. Melting behaviour was examined by heating microscope. Results obtained from heating microscope measurements after adding the bentonite can be seen on (Fig.1b) for blue, on (Fig.1c) for yellow and on (Fig.1d.) for grey clay Image analysis revealed the characteristic temperatures (T) and height expansion (H) of clay samples produced with 5 %, 10 % and 20 % of bentonite material (Fig. 1b.). The maximum height expansion of the blue, grey and yellow clay samples without bentonite were 138 %, 123 % and 122 %, respectively. Expansion started at blue clay sample at 1220°C, at yellow clay at 1253°C while grey clay at 1250°C (Fig. 2a). Relation between maximum height expansions, which related to 10 % of bentonite of clay samples as a function of temperature illustrated on (Fig.2b), while relevant data from results summarized in Table 1. Addition of 10 % bentonite elevated in highest rate the expansion of samples and shifted beginning temperature of the expansion process.

Figure 1. a) Chemical composition of the technological sample as plotted on Riley's diagram (1951). b) Heating microscope photographs and relevant values for blue clay with bentonite. c) Yellow clay with bentonite. d) Grey clay with bentonite

Figure 2. a) The relation between height expansion of clay with temperature before adding bentonite b) after adding 10% of bentonite
Table 1. Maximum height expansion (MHT) and sintering temperature (ST) for the clay samples

| Sample | Bentonite 0 % | Bentonite 5 % | Bentonite 10 % | Bentonite 20 % |
|--------|--------------|-------------|-------------|-------------|
|        | ST  | MHE | ST  | MHE | ST  | MHE | ST  | MHE |
| B      | 1220 | 138 | 1230 | 128 | 1190 | 164 | 1204 | 150 |
| Y      | 1253 | 122 | 1250 | 111 | 1240 | 133 | 1235 | 125 |
| G      | 1250 | 123 | 1235 | 131 | 1245 | 135 | 1240 | 132 |

3.2 Properties, mineral phases and microstructure of expandable clay with bentonite

For selecting of a lightweight aggregate, bulk density is one of the most crucial parameter. The results were summarized in Table 2. Bentonite affected the ranges of bulk density and compressive strength of aggregates (Fig 3 a, b). Bulk density and compressive strength range of the Mályi clay samples with 0 % of bentonite was in (0.57-1.2) g/cm$^3$ and (1.11-4.82) MPa respectively at 1225°C. The compressive strength values were higher, than 1 MPa, so they are acceptable according to [32, 33] as LWA. Whilst the range of bulk density and compressive of aggregates with 5% of bentonite were (0.6-0.96) g/cm$^3$ and (2.45-8) MPa respectively, 10% of bentonite were (0.55-0.95) g/cm$^3$ and (3-7.15) MPa and with 20% of bentonite were (0.82-1.00) g/cm$^3$ and (3.8-8.41) MPa respectively, at 1225°C (Table 2). Fig. 3 b shows the enhancement in compressive strength at all samples with 5%, 10% and 20% of bentonite.

Table 2. Bulk density and compressive strength of expanded clay aggregates at different temperature

| Sample | Bentonite 0 % | Bentonite 5 % | Bentonite 10 % | Bentonite 20 % |
|--------|--------------|-------------|-------------|-------------|
|        | Bulk density, g/cm$^3$ | 1175 | 1200 | 1225 | 1225 | 1225 | 1225 | 1225 |
| B      | B             | 1.2 | 0.72 | 0.57 | 0.94 | 0.77 | 0.6 | 1.02 | 0.87 | 0.55 | 1.21 | 0.92 | 0.82 |
| Y      | B+G (50-50)  | 1.35 | 1.07 | 0.86 | 1.02 | 0.93 | 0.84 | 1.08 | 0.93 | 0.85 | 1.03 | 0.92 | 0.87 |
| B+Y (50-50) | G             | 1.4 | 0.8 | 0.63 | 1.18 | 1.01 | 0.9 | 1.1 | 1.07 | 0.92 | 1.21 | 1.16 | 0.95 |
| G      | 1.5 | 0.95 | 0.84 | 1.13 | 1.02 | 0.77 | 1.13 | 0.98 | 0.79 | 1.12 | 0.94 | 0.85 |

Compressive strength, MPa

| Sample | Bentonite 0 % | Bentonite 5 % | Bentonite 10 % | Bentonite 20 % |
|--------|--------------|-------------|-------------|-------------|
| B      | 6 | 2.96 | 1.54 | 6.7 | 10.4 | 2.45 | 9.6 | 8.5 | 3.27 | 9.23 | 5.4 | 3.8 |
| Y      | 31 | 6 | 4.82 | 11.7 | 12.2 | 8 | 16.5 | 9.47 | 7.15 | 17.7 | 11 | 8.41 |
| B+G (50-50) | 20 | 2.5 | 2.22 | 9 | 6.9 | 3.2 | 13.9 | 4.91 | 3 | 10.3 | 5.99 | 4.5 |
| B+Y (50-50) | 25 | 4.1 | 1.11 | 12.7 | 9.63 | 3.5 | 14 | 8.59 | 4.2 | 9.42 | 7.62 | 4.75 |
| G      | 27 | 2.46 | 2.09 | 18.6 | 8.4 | 2.62 | 16 | 9.2 | 4.32 | 14.1 | 8.18 | 4.31 |

Figure 3. a) Bar chart of bulk density of expanded clay aggregates at 1225°C
b) Bar chart of compressive strength of expanded clay aggregates at 1225°C
Mineral phases before and after firing were studied by XRD and SEM. The mineral phases formed at 1225 °C were quite different from the pre-firing stages. The mineral phases of blue clay sample were quartz (pdf no. 01-079-1910), hematite (pdf no. 01-073-0603), and anorthite (pdf no. 01-073-0265) whilst detectable phases in yellow clay sample were quartz, hematite, anorthite and mullite (pdf no. 01-083-1881). On the other hand, adding bentonite to the different types of expanded clay was led to change in the mineral phases of the aggregates compared to pure clays. Not only bentonite had great influence on the aggregates, but also, the temperature was a crucial factor for changing in the mineral phases. In this section, we will focus on the aggregates with 5% and 10% of bentonite, because the lowest density, maximum height expansion and high compressive strength were experienced. Firing samples with 5% of bentonite at 1200 °C, mineral phases of clay with 5% of bentonite were hematite and quartz low (pdf no. 01-085-0335). Mineral phases of blue clay aggregates were hematite, quartz low and hercynite (pdf no. 01-089-1683) (Fe^{2+}Al_{2}O_{4}) (Fig. 4b) after firing this clay samples with 10% of bentonite at 1200 °C. At 1225 °C, blue clay with 5% of bentonite was consisted of mullite, hematite, quartz low and quartz, whilst yellow clay with 5% of bentonite included hematite, and quartz low. Blue clay with 10% of bentonite contained mullite, Na anorthite, hematite and quartz low (Fig. 4b).

**Figure 4. XRD patterns of a) LWCAs with 5% and 10% of bentonite fired at 1200°C b) LWCAs with 5% and 10% of bentonite fired at 1225°C**

Microstructure determinates the properties of LWAs. Reduction of porosity caused an increase in density and compressive strength. On the other side, a regular pore size can increase the compressive strength of LECA because it gives a more homogenous stress distribution throughout the microstructure [34, 35]. Microstructure, shape and arrangement of the pores in expanded clay aggregates with 10% of bentonite (1225°C) can be observed on SEM images (Fig.5). Addition of 10% bentonite to clay increased the compaction of aggregates and closed the pores. Shape of the pores altered relative to pure clay i.e. roundness of the pores was increased and size of it decreased (Fig. 5). Observation of cross-section of aggregate expanded from blue clay pellet (Fig. 5a) revealed that aggregate composed of two layers, an inner and outer layer. Outer layer built up smaller pores than the inner layer while inner layer had one large pores. After adding 10% of bentonite, microstructure of the aggregates included just one layer with irregular pores with white patches. Size of pores were smaller than size of pores in samples without bentonite (Fig. 5b) and surface of the aggregates was much smoother than experienced at expanded pure clay samples. White patches were surrounded the pores (Fig.5 b, c, d). Chemical analysis with EDAX for these patches revealed that its main phase consists of iron with lower amount of silicon and alumina.

**4. Discussion**

Addition of bentonite to clay samples had great effect on expansion, sintering point, bulk density and compressive strength of lightweight expanded clay aggregates. After firing at 1225°C, height expansion, bulk density and compressive strength of the blue clay sample with 10% of bentonite were 164%, 0.55 g/cm³ and 3.27 MPa respectively. Comparing to expanded pure clay samples, there is a great enhancement in height expansion by 68%, in compressive strength of the aggregates by 112% and the
bulk density was also lower by 5%. These high values traces back to the changing in mineral phases. According to XRD, sample (10% bentonite) had mullite mineral phase at 1225°C, which was one of the most important phase affected the compressive strength of the aggregates, while anorthite mineral phase was another factor that controlled the expansion of aggregates. Compressive strength of the blue clay aggregates with 10% of bentonite at 1200°C was around 8.5 MPa, which is a high value. Hercynite phase formed at this temperature, which could cause an increase in compressive strength because of its Mohs hardness (7.5) and specific gravity (4.5). However, at 1225°C, hercynite mineral phase didn’t exist. Therefore, when the temperature increase the mineral phases were changed and the bulk density and compressive strength of the aggregates was decreased. On SEM images of clay aggregates with 10% of bentonite, patches of iron element were found, and pores surrounded by these patches. These were formed when the expansion increase generated higher expansion of the aggregates with 10% of bentonite up to 164% (Fig.5b). On the other hand, no patches found on the aggregates with 5% of bentonite. Expansion of the aggregates with 5% of bentonite was decreased, so the volume of pores was low. Height expansion, bulk density and compressive strength of yellow clay sample with 10% of bentonite were 133%, 0.95 g/cm³ and 7.15 MPa respectively, after firing at the 1225°C. Comparing to pure clay samples, enhancement rate in value of height expansion was 50%, compressive strength of the aggregates was with 48% higher and bulk density by 20% higher lower. According to XRD results, this sample had mullite phase (3.05 g/cm³), which had effect on the compressive strength of the aggregates, so the yellow sample had the highest compressive strength value of 7.15 MPa at 10% of bentonite content. Whilst, the anorthite mineral phase did not exist, so the height expansions of samples were low.

5. Conclusion
Addition bentonite material to the clay samples has great effect on the bulk density, sintering and melting point and compressive strength of the aggregates. In addition, the different amount of bentonite (5%, 10% and 20%) that added to clays enhanced the compressive strength of the aggregates by 48% to 112%. The most crucial values of addition of bentonite is 10% because all the properties of LWA were better and bulk density of the aggregates decreased by 5% to 20% compared with the other added amount of bentonite. Besides. hercynite mineral phase was one of the phases can be controlled in compressive strength of the aggregates due to its Mohs hardness of 7.5. Beside, this phase can increase bulk density of the aggregates because the of its own density value of 3.95 g/cm³. Anorthite minerals is that plays a role in the expansion of the aggregates. Finally, Bentonite material can be used as additive.
to the aggregates where there is a demand to enhance the compressive strength and expansion of the aggregates.

Acknowledgement
This research was supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry.

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