

MODIFICATION OF THE LIGHTWEIGHT AGGREGATE WITH THE USE OF SPENT ZEOLITE SORBENTS AFTER THE SORPTION OF DIESEL FUEL

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The paper presents the investigation of lightweight aggregate that can be obtained from the mass of raw material modified by clay minerals, zeolites and waste. In this experiment it was modified by zeolites – clinoptilolite and Na-P1, which were used for the removal of diesel fuel. That kind of substances can get into the environment in an uncontrolled way causing the ecological risk. The spent sorbent containing fuel constitutes waste, which should be utilized. This process prevents petroleum substances from reentering to the environment. The spent zeolite (10%) was added to the clay (90%) originated from “Budy Mszczonowskie” bed. Homogenization process consisted in mixing the ingredients with water until a plastic consistency was formed. The formed beads of coarse fraction of 8-16 mm were dried for 2h in a laboratory oven at 110 °C and then fired at 1170 °C. The obtained aggregates were tested on the basis of appropriate standards in order to determine their physical and mechanical properties. The research indicates that the lightweight aggregate obtained from clay and zeolites used for the removal of petroleum compounds is a valuable building material. The porous structure of each bead, closed with durable ceramic coating, provides the aggregate with a lot of functional properties.

Key words: lightweight aggregate, modified by zeolites, petroleum compounds.

Подано дослідження легкого заповнювача, який можна одержати із суміші сировинних матеріалів, модифікованих глинистими мінералами, цеолітами і відходами. У цих експериментах використано модифікований цеоліт - клиноптилоліт і Na-P1, що застосовувалися для видалення дизельного палива. Такі речовини можуть потрапити в навколишнє середовище і неконтрольовано викликати екологічні ризики. Відпрацьований сорбент, що містить як компонент відходів паливо, повинен бути утилізований. Цей процес запобігає повторним викидам нафтопродуктів у навколишнє середовище. Відпрацьований цеоліт (10 %) додавали до глини (90 %) родовища "Budy Mszczonowskie". Процес гомогенізації полягав у змішуванні інгредієнтів з водою до потрібної консистенції. Сформовану фракцію грубого заповнювача 8–16 мм висушували протягом 2 год у лабораторній печі при 110 °C і потім випалювали при 1170 °C. Отримані легкі заповнювачі випробовували на основі відповідних стандартів, щоб визначити їх фізичні та механічні властивості. Дослідження показують, що легкий заповнювач, отриманий з глини і цеолітів, може використовуватись для видалення нафтових сполук і є цінним будівельним матеріалом. Пориста структура кожного зерна, покрита довговічним керамічним покриттям, забезпечує одержання заповнювача з великою кількістю функціональних властивостей.

Ключові слова: легкий заповнювач, модифікований цеоліт, нафтові сполуки.

Introduction

LECA is a well-known lightweight aggregate which is formed by the thermal treatment of minerals by firing at temperatures up to 1300°C. Materials as clay, expanded perlite or vermiculite are convenient starting materials for the production of lightweight aggregates [Decler J. Viaene, 1993; Dermirdag S.,

Gunduz L. 2008]. Artificial lightweight aggregates are formed by rapid heating at high temperature of materials that have the ability to expand.

Two conditions are necessary to achieve an appropriate expanded material (Riley, 1951):

1. It must contain substances that release gases at high temperature (T_1),
2. A plastic phase with the appropriate viscosity must be produced so it can trap released gases at temperature T_1 .

Lightweight aggregates characterized by low bulk density not exceeding 1200 kg/m^3 or by particle density not exceeding 2000 kg/m^3 [UNE EN-13055-1, 2003], and porosity remains within the range of 80% represented mainly by the closed pores, which are surrounded by glass coating resulting from the thermal transformation of clay minerals. Due to their typically low density, good thermal, physical and mechanical properties, acoustic insulation, lightweight aggregates have become a focus of interest. In fact, they are essential components in a variety of building materials such as prefabricated structural units, lightweight concretes; especially in high rise buildings; as well as track ballasts and road coatings, along with bituminous materials and other geotechnical applications [Bodycomb F. M., Stokowski S. J. , 2000; Fakhfakh E. et al. 2007; Gonzales –Corrochano et al. 2010].

In recent years modifications of the fiber composition of mixtures by using different waste dry as glass [Kralj D., 2009; Wei Y.-L. et al., 2011], fly ash [Sokolova S.N., Vereshagin V.I., 2010; Kockal N.U., Ozturan T., 2011], sewage sludge [Anderson M., Skerratt R.G., 2003], spent absorbents [Franus et al. 2011] and other wastes [Gonzales –Corrochano B., 2009; Libre N.A. et al. 2011] have been observed.

Increasing generation of waste is one of the main environmental problems in industrialized countries. The European Union is attempting to restrain this increasing generation through legislation. Poland has been under the European legislation for many years and the problem has still not been resolved. One of the types of waste are used sorbents after the sorption of petroleum compounds. These sorbents, according to the Ordinance, are qualified as waste, which is eliminated through biodegradation or combustion. Combustion is an expensive method, due to the high demand of heat can cause problems in complying with the standards on the emissions of greenhouse gases. Additionally, the combustion process generates fly ash as by-product.

The aim of this study is to obtain a lightweight aggregates using minerals such as clinoptilolite and synthetic zeolite NaP1 which were used in sorption of petroleum substances.

Materials and methods

Characteristics of starting material

Natural zeolite clinoptilolite was obtained from the mine Sokyrnytsya (Transcarpathian Region, Ukraine). The mineral was pulverized in a crusher and divided into fractions, so-called "powder" (0.2 - 0.5 nm) that was used for further study.

Material type Na-P1 was obtained in the hydrothermal fly ash conversion process with sodium hydroxide, using a processing line for the production of zeolites from fly ash according to the reaction:



In one cycle of the synthesis of zeolite Na-P1 falls in a pilot-scale 20 kg of ash, 12 kg NaOH and 90 dm^3 of water. The temperature and duration of the process amounts to 80°C and 36 h (Wdowin et al. 2014).

Clay was collected after direct excavation of the deposit, which is currently operated by the Company Aggregate Light "Expanded clay".

Chemical composition of raw materials was determined by the XRF method. The Philips PW 1404 spectrometer was applied. An XRD lamp with double anode (Cr-Au) with a maximum power of about 3 kW constituted the induction source.

S_{BET} specific surface area of the zeolite materials was determined with the use of N_2 low temperature adsorption/desorption method, based on the theory of multilayer adsorption Brunauer-Emmett-Teller (BET) at p/p_0 between 0.06 and 0.3. Measurements were made by ASAP 2020 Micromeritics.

Verva ON diesel oil, which was bought at the PKN Orlen gas station, was used in the study. Oil density was determined by a pycnometry method, and its value was 0.833 g/cm³. The dynamic viscosity of the oil was determined according to DIN 53453, and its value was $3,6 \cdot 10^{-8}$ Pa·s.

Sorption of petroleum substances

Zeolites clinoptilolite and Na-P1 were used as potential sorbents of petroleum substances. For this purpose the maximum sorption capacity in relation to diesel Verva ON (PKN Orlen) was determined. Then, the oil was mixed with the sorbent in a ratio that allowed for the highest adsorption of oil substance, without exceeding the maximum sorption capacity. It is essential because used mineral sorbent should not return the sorbed substance, for example under the impact of pressure. Moreover, in order to use this kind of waste in the lightweight aggregate production, it should be in a solid compact form, which is suitable for plastic forming. In order to remove petroleum substances, 1 kg of mineral sorbent and 0,25 kg of oil were used in case of clinoptilolite, and 1 kg of sorbent and 0,5 kg of oil were used in case of Na-P1. These proportions allowed to obtain waste materials, which are appropriate substrate for lightweight aggregate manufacturing.

Lightweight aggregate preparation

The clay was dried in 105°C and grinded in the mortar to the fraction of < 0,063 mm. After oil sorption, zeolite wastes were mixed with the clay in a ratio of 9:1 (clay: used clinoptilolite was named *CC*, and clay: used Na-P1 was named *CNa-P1*) and moulded with distilled water to the plastic consistence. From this moulding mixtures, lightweight aggregate spheres with diameters in the range of 8-16 mm were formed manually, and then were calcinated for 30 minutes in the laboratory furnace SM-2002 "Czylok" in the temperature of 1170°C. After calcination, the samples were left in the furnace until their cooling to 100°C.

Properties of lightweight aggregates

The physical, mechanical, mineralogical and structural properties of obtained lightweight aggregates *CC* and *CNa-P1* were determined. Loos bulk density (ρ_b , expressed in g/cm³) of lightweight aggregate was estimated in accordance with the standard UNE-EN-1097-3(1999). Particle density (*apparent* and *dry*, expressed in g/cm³) and water absorption after 24 h (WA_{24h}) of aggregate immersion were determined with the use of an established procedure described by the standard UNE-EN-1097-6 (2000). According to this norm:

- *Apparent particle density* (ρ_a) is the relationship between the mass of a sample of aggregates dried in an oven and the volume these aggregates occupy in water, including the watertight internal pores and excluding available pores to water.

- *Dry particle density* (ρ_d) is the relationship between the mass of a sample of aggregates dried in an oven and the volume these aggregates occupy in water, including the watertight internal pores and the available pores to water.

The void percentage (H) (air space between aggregates in a container) and porosity (P) were estimated using the method specified in the standard UNE-EN-1097-3 (1999) and calculated according to the following equations:

$$H = 100 \cdot (\rho_d - \rho_b) / \rho_d$$

$$P = \rho_d - \rho_a / \rho_d$$

where: H is the void percentage (%), P is porosity (%), ρ_b is the bulk density and ρ_d is the dry particle density of the sample.

The investigations of the material compressive strength were conducted according to the standard PN-78/B-06714/40. The investigation consisted in estimating the percentage of loss of the aggregates particles mass as a result of crushing. The value of determination is a resistance to crushing (X_r) which was estimated in accordance of the equation:

$$X_r = m - m_1 / m \cdot 100$$

where: m – the mass of the samples before examination (g); m_1 – the mass of the sample after examination (g).

Frost resistance of the aggregates was determined on the basis of the standard UNE-EN-1367-2(1999). It expresses the maximum permissible percentage loss of the mass of aggregate; which was soaked with water and subjected to a cyclic freezing to the temperature of -17,5 °C (10 cycles) and defrosting at the temperature of 20 °C.

Determination of colouring compounds was conducted in accordance with the standard PN-88/B-06714/36. For this study, the lightweight aggregates fraction of 0,5-0,8 mm, from which two samples of 100 g were taken, was used. The samples were washed with distilled water and dried to dry mass. In the next step the samples were weighted and put into filter paper with a diameter of 25 cm. The filters with lightweight aggregates were placed in the cotton bags that were tied and saturated with distilled water. Then, beakers were filled up to ¼ of the volume with distilled water and the bags with lightweight aggregates were dipped there so as the water could cover it with a layer of few centimeters. The samples were kept in a state of slight boiling for 16 h. After that time, the bags with LECA were dried, the aggregates were removed from them, then the bags dried slightly again and the coloured stains were observed.

Mineralogical analysis for obtained aggregates were conducted in order to identify the mineral phases present in investigated materials and to estimate their amount as well as to determine the interplanar distances of the crystal framework. The examination was performed with the use of a Philips X'pert APD diffractometer with PW 3020 goniometer, Cu lamp and a graphite monochromator.

The surface morphology of the main mineral components of the starting materials as well as of the obtained lightweight aggregates were analyzed by the scanning electron microscope (SEM) FEI Quanta 250 FEG. With the use of high-temperature microscope the characteristic temperatures of lightweight aggregates were determined. The samples - raw material mixtures - after being mixed with water and squeezed in a hand press (to obtain a cylindrical shape, 3 mm in diameter and 3 mm high) were subjected to the thermal processing. The temperature gained in the high-temperature microscope reached up to 1100°C – 30 °C/1min and over 1100°C – 10°C/1min. The experiment was performed in an oxidation atmosphere in the temperature starting from 760 °C and up to the maximum temperature of the high-temperature microscope – 1500 °C.

Results and discussion

Characterization of the starting materials

The chemical composition analysis, performed with the use of XRF method, indicates the significant amount of SiO₂ (68,02%) and Al₂O₃ (12,92%) in clinoptilolite and 37,93% SiO₂ and 18,83% Al₂O₃ in Na-P1 (Table 1).

Table 1

Chemical composition of clinoptilolite and synthetic zeolite Na-P1

Component	Clinoptilolite %	Na-P1 %
Na ₂ O	0,69	6,57
MgO	0,75	1,15
Al ₂ O ₃	12,92	18,83
SiO ₂	68,02	37,93
P ₂ O ₅	0,16	0,31
SO ₃	0,09	0,25
K ₂ O	3,36	1,00
CaO	3,71	14,41
TiO ₂	0,20	0,83
MnO	0,06	0,08
Fe ₂ O ₃	2,11	5,09
LOI	8,57	13,89

The presence of K₂O, CaO, Fe₂O₃, Na₂O, and MgO in the zeolite materials was denoted in lower quantities. The chemical composition analysis for clay material (Table 2) shows that it contains significant amount of SiO₂ and Al₂O₃, alkaline earths oxides K₂O, Na₂O, MgO, CaO, and Fe₂O₃.

Table 2

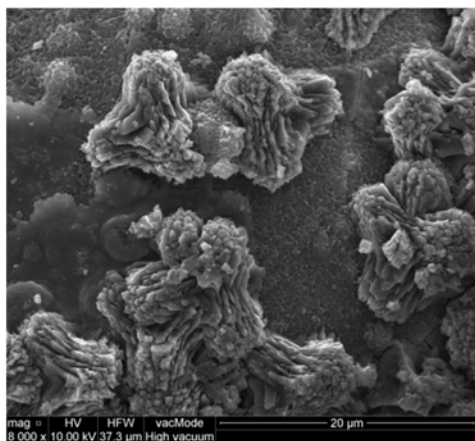
Chemical composition of clay from “Mszczonów”

Element	Content [%]
SiO ₂	67,50
Al ₂ O ₃	14,30
Fe ₂ O ₃	5,60
MgO	2,40
K ₂ O	1,37
Na ₂ O	0,72
CaO	0,32
TiO ₂	0,22
BaO	0,02
MnO	0,01
ZnO	0,03

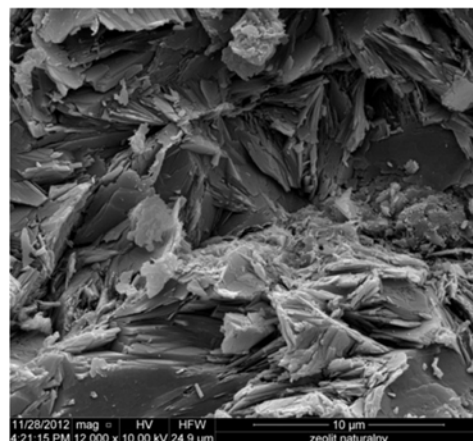
The presence of oxides in the starting materials for manufacturing ceramic sinters contributes to the formation of liquid phase, which influences the viscosity of the ceramic mass and it decreases its swelling temperature (Riley CH. 1950).

Specific surface area S_{BET} determined on the basis of N₂ adsorption/desorption isotherm is 18,2 m²/g for clinoptilolite and 86,8 m²/g for Na-P1.

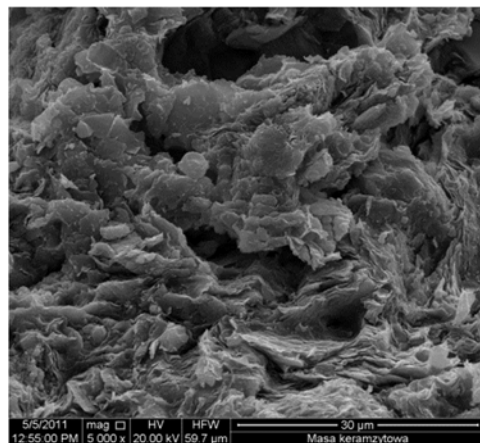
Detailed analysis of morphology of the tested materials showed that clinoptilolite crystallites exhibit scaly habit. They create aggregates in a lamellar and needle-like forms in a size of 20-30 μm. Na-P1 material are being formed in a specific bundles with scaly habit (Figure 1).



Na-P1



Clinoptilolite



Clay

Fig.1. SEM images of the starting materials; clay, clinoptilolite and Na-P1

Estimation of the petroleum substances sorption capacity

The maximum sorption capacity of clinoptilolite and Na-P1, determined on the basis of Westinghouse method, were 0,46-0,49 g/g and 1,00-1,20 g/g, respectively. The differences in the amounts of sorbed oil per mass unit of this two sorbents, ensue from the differences in specific surface areas of both materials. The synthetic zeolite is characterized by higher S_{BET} than the natural clinoptilolite. Therefore, it could sorb the petroleum substance over twice as much.

Properties of Lightweight aggregates

The lightweight aggregates, obtained from used sorbents and clay from Mszczonów, and calcinated in temperature of 1170 °C are presented in Figure 2.



Fig. 2. Images of the obtained lightweight aggregates, calcinated in temperature of 1170°C (CC) – below, (CNaPI) – above

The lightweight aggregate CNaPI is more porous, has visible glasslike coating and is lighter than aggregate CC. The results of bulk density investigation report that this value is 2630 kg/m³ for CC and 2590 kg/m³ for CNaPI, calcinated in 1170°C (Table 3). This values are typical for this kind of lightweight aggregates.

Table 3

Determined parameters of lightweight aggregates

Parameter	Lightweight aggregate CC	Lightweight aggregate CNaPI
Dry particle density, ρ_d (kg/m ³)	2790	2740
Apparent particle density, ρ_a (kg/m ³)	940	868
Bulk density, ρ_b (kg/m ³)	540	494
Water absorption (%)	10.00	11.5
Void, H (%)	80	82
Porosity (%)	66	68
Frost resistance, F (%)	0.08	1
Resistance to crushing, X_r (%)	15	28

Particle density of the tested aggregates was 260 kg/cm³ (CC) and 1170 kg/cm³ (CNaPI), whereas bulk density – 260 kg/cm³ and 1170 kg/cm³ for CC and CNaPI, respectively. As the temperature increases,

the *CC* and *CNaPI* particle density decreases due to two main reasons: the formation of lower-viscosity viscous layer and generation of more bloating gas (Wei Y.-L. et al. 2011). The particle density values obtained for all the artificial aggregates are less than 2000 kg/m^3 ; therefore, all the artificial aggregates manufactured in this study are classified as lightweight aggregates according to the standard UNE-EN-13055-1 (2003).

Water absorbability of *CC* equals 10%, whereas of *CNaPI* – 11,5%. This slight escalation of water absorbability, probably ensued from the escalation of open porosity of grains and higher heterogeneity of their shape. Slightly less values of water absorbability of the tested aggregates arise from the presence of glass phase, which is observed especially in *CNaPI*, in a form of a coating. A particle with isolated pores or a vitrified surface tends to absorb little water, whereas one with connected or open pores will absorb water like a sponge (Huang and Hwang, 2007). The resulting value of water absorbability of the obtained aggregates is comparable with the values of water absorbability of commercial aggregates Lytag, which is 17%. What is more, the particle density of aggregate Lytag ($1,34 \text{ kg/m}^3$) is similar to the particle density of the aggregates modified with used sorbents. Generally acceptable water absorption capacity based on 24-h soaking in water is lower than 20%.

The porosity of examined aggregates was 66% and 68% for *CC* and *CNaPI* respectively. The value of this parameter for commonly produced LECA is within the range of 20-50%. This value is responsible for an appropriate water absorbability, high diffusivity of water vapor, thermal and acoustic insulating power. Investigation of coloring compounds showed that paper filters had not been colored in any way, which means that the lightweight aggregates *CC* and *CNaPI* would not color other ceramic materials. The results are presented in Figure 3.

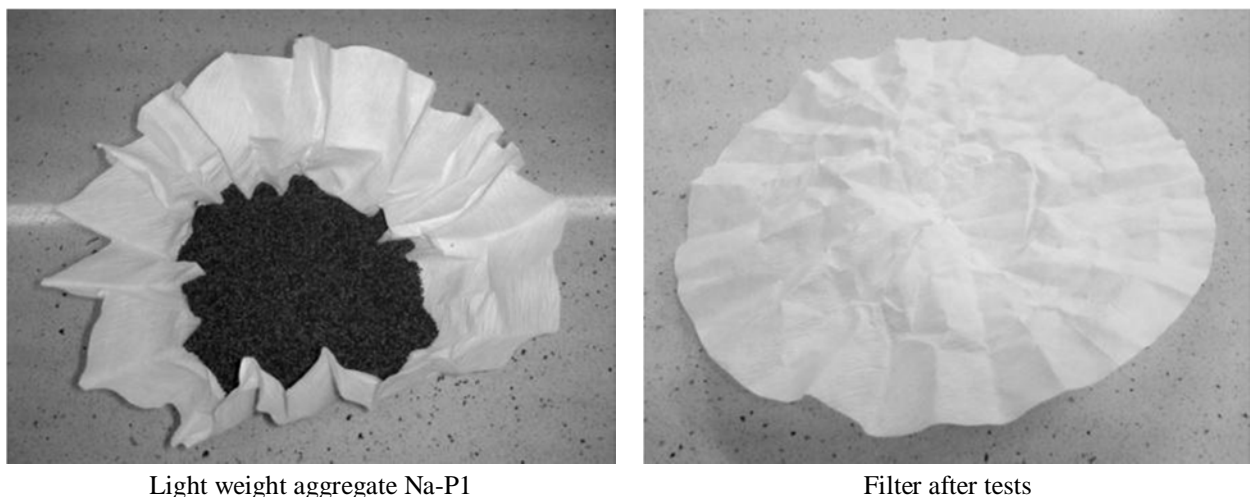


Fig. 3. Filter paper with *CNaPI* before and after investigation of colouring compounds

Resistance to crushing X_c of *CC* is 15% and for *CNaPI* is 28%. When it comes to this index value for concrete, it should not exceed 16% for the aggregates used for LB 25 class of concrete and 28% for the aggregates used for concrete with the class below LB 25 (presently LC 20/22).

Frost-resistance of aggregate does not exceed 1%. The aggregate grain did not show any occurrence of cracks after the test. The aggregate is characterized by the high porosity and large pore sizes. Water penetrating the grain probably has not filled in the whole surface of pores; therefore, it did not cause any damage to aggregate after freezing.

XRD patterns of tested lightweight aggregate are presented in Figure 4.

Main mineral components of clay from "Budy Mszczonowski" bed are clay minerals represented by beidellite, illite and which are accompanied by quartz in minor amounts.

In the mineral composition of obtained aggregate, glasslike phase is domain, which was detected by the characteristic background increase of diffraction patterns within the angular range of 15-35 (2θ). Furthermore, the mineral composition is accompanied by mullite and hematite.

SEM images of the aggregates *CC* and *CNaPI*(Figure 5) present porous structure of the materials. Pores have a diversified shape and size. Nevertheless, the spherical shape of pores is dominating, they are accompanied with small amount of irregular shaped pores. Texture of the granules of the materials is compact, with the presence of small pores, whose sizes are within the range of 5-20 μm .

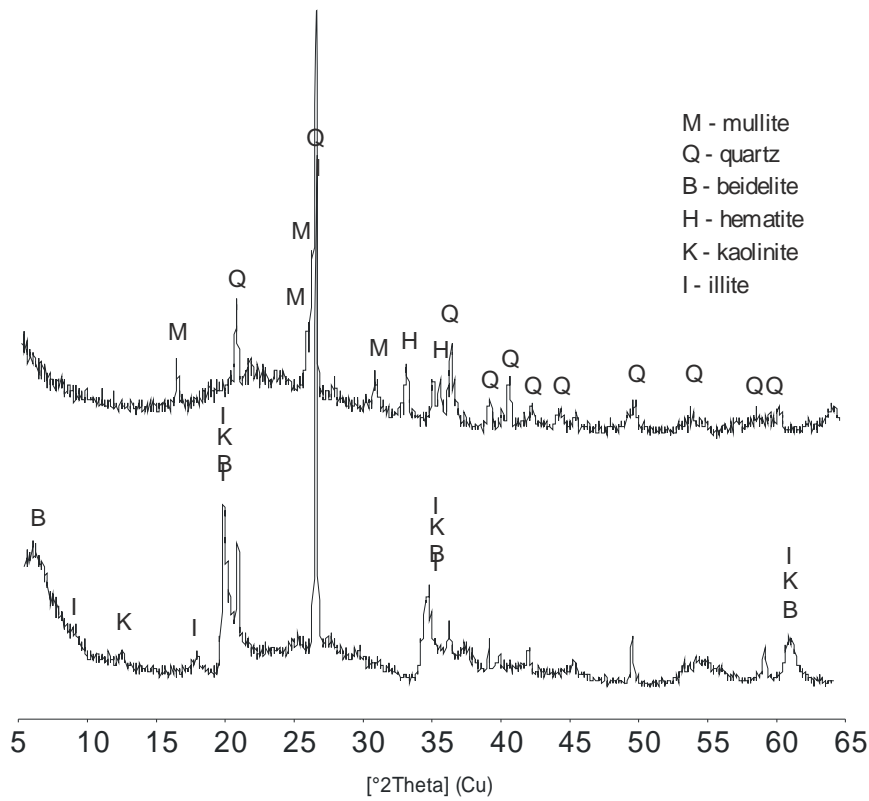


Fig. 4. XRD patterns of lightweight aggregate

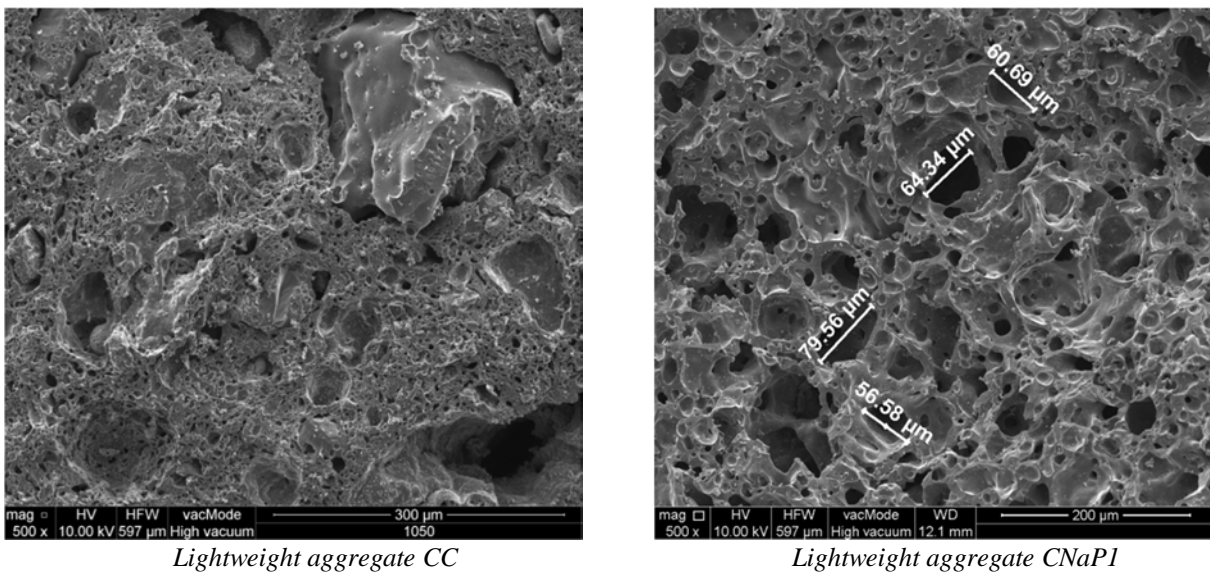


Fig. 5. SEM images of *CC* and *CNaPI* granules microsection

The lightweight aggregate *CNaPI* possesses considerably greater pores within the range of 10-80 μm . Moreover, granule interior exhibits numerous pores which have favorable impact on the decrease of particle density of the material.

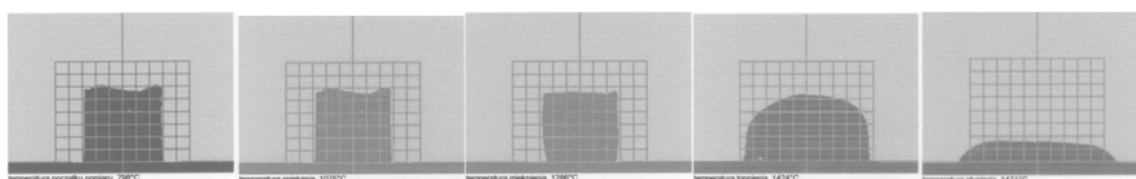
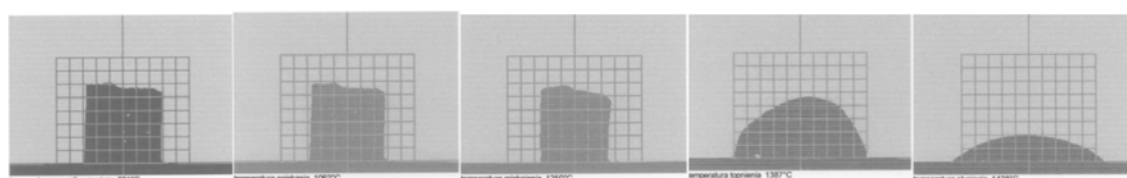
Lightweight aggregate investigation with the use of high temperature microscope allowed to determine their typical temperatures. The temperature of beginning and maximum sintering, the softening temperature, melting point and flow temperature of *CNaPI* are higher than for *CC* (Table 4).

Table 4.

Characteristic temperatures of aggregates (°C): T_1 =beginning of sintering, T_2 =maximal sintering point, T_3 =softening point, T_4 =melting point, T_5 =flow temperature, T_2-T_1 ; T_3-T_2 = intervals – thermal wide suitable for firing

Aggregate	T_1	T_2	T_3	T_4	T_5	T_2-T_1	T_3-T_2
<i>CC</i>	718	1075	1286	1424	1471	357	211
<i>CNaPI</i>	718	1062	1250	1387	1428	344	188

Changes of the size of samples in the temperature of beginning and sintering are the effect of thermal changes in the minerals, which constitute the composition of the aggregates (clay mineral dehydration, dehydroxylation, organic substances oxidation, carbonates dissociation). This thermal changes produce solid and vapor phase, which are emitted out the porous sample. (Figures 6 and 7).

Fig. 6. High-temperature microscope images of *CC*Fig. 7. High-temperature microscope images of *CNaPI*

In softening temperature, in heated samples a liquid phase is forming, where eutectic solutions are the source of that phase in a multicomponent aluminosilicate system, with participation of K_2O , Na_2O , CaO , MgO , FeO . While evaluation of the technological parameters of calcinated aggregates, the maximum sintering temperature is a limit of safety calcination, and the wide interval between the maximum sintering temperature and softening temperature does not threaten with a complete degradation of the aggregates during calcination.

Conclusions:

1. Natural zeolite clinoptilolite and synthetic zeolite Na-P1 are efficient mineral sorbents for the removal of petroleum substances.
2. Lightweight aggregates *CC* and *CNaPI*, obtained on the basis of clay from Mszczonów and modified with used sorbents that were applied for petroleum substances removal, exhibit physical and mechanical parameters appropriate for lightweight aggregates. Therefore, they can be used in the lightweight concrete production, from which the blocs for the construction of load bearing walls and partition walls, flooring and ventilation blocks, thermal insulation of floors and slab roofs are made of. *CC* and *CNaPI* exhibit porous structure with diversified shapes and size. *CNaPI* possesses significantly greater pores than *CC*. Both of them has glassy surface, which constitutes a desirable attribute of lightweight aggregate. Thermal characteristic parameters of *CNaPI* are higher than the parameters of *CC*. It could result from the highest amount of sorbed oil in starting material – used Na-P1.
3. The addition of waste materials such as used sorbents after the removal of petroleum substances in the production of lightweight aggregate is advantageous for two reasons – it is a way to utilize the hazardous waste, and improve the properties of obtained aggregate.

Acknowledgment

This research was financed by NCBiR within the Project No. PSB1/A2/7/2012 and the Project No IPBU.01.01.00-06-570/11-00.

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