

The use of spent glauconite in lightweight aggregate production

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The presented work has shown an application of spent glauconite bed after purification of wastewater for production of lightweight expanded clay aggregates. Sewage, from which it was removed Zn ions, came from technological line (zinc-works) of Communication Equipment Factory „PZL” Świdnik. Spent glauconite bed was used as an additive in lightweight aggregate production which was obtained using plastic method by sintering, at temperature 1140°C and 1200 °C, of spent glauconite amounts 10, 15, 20 and 25% wt. with clays from open-cast mine „Budy Mszczonowskie”. The presence of the mineral improves sinter texture, increases porosity and contributes to formation of glassy layer on the surface of the aggregates. Tests of zinc elution from lightweight of aggregate samples has shown very low mobility of zinc ions. Content of zinc in water extracts obtained from lightweight of aggregate is definitely lower than zinc concentration permitted for sewage discharge to water or soil, means that spent material is not offensive for the environment as it can be used as a high quality building product.

Keywords: glauconite, pickle wastewater, lightweight of aggregate, utilization of wastes

El uso de glauconita gastada en la producción de agregados ligeros

El trabajo presentado ha demostrado una aplicación de agotado depósito de glauconita después de la purificación de aguas residuales para la producción de áridos ligeros de arcilla expandida. Las aguas residuales, de la que fueron eliminados los iones Zn, vinieron de la línea tecnológica del equipo de comunicación de la fábrica “PZL” Świdnik. Agotado depósito de glauconita se utiliza como aditivo en la producción de áridos ligeros que se obtuvo utilizando el método de plástico de la sinterización, a temperatura C. 1140 ° y 1200 ° C, de spent glauconita amounts 10, 15, 20 y 25% en peso. con arcillas de la mina a cielo abierto “Budy Mszczonowskie”. La presencia de este mineral mejora la textura de sinterización, aumenta la porosidad y contribuye a la formación de la capa vítrea en la superficie de los agregados. Pruebas de elución de zinc a partir de las muestras de áridos ligeros ha demostrado la movilidad muy baja de iones de zinc. Contenido de zinc en los extractos acuosos obtenidos a partir de áridos ligeros es definitivamente menor que la concentración de zinc permitido para la descarga de aguas residuales al agua o al suelo, significa que el material usado no es ofensivo para el medio ambiente ya que puede ser utilizado como un producto de alta calidad de la construcción.

Palabras clave: glauconita, aguas residuales de la salmuera, áridos ligeros, utilización de desechos

1. INTRODUCTION

Glauconite is a clay mineral which due to numerous specific surface properties is useful in capturing contaminants in the form of heavy metal cations from aqueous solutions [1-9].

Minerals of this group are quite commonly used in laboratory experiments for the removal of heavy metals from aqueous solutions, mainly in the ion-exchange process [10-14].

Spent ion-exchange deposits of glauconites transform into waste which because of their negative chemical and biological properties require special treatment. This involves specific capital investments and appropriate support to carry out the processes. One of the methods employed in utilization of hazardous waste is the immobilization of waste into ceramic aggregate [15].

However, glauconites are rarely used on an industrial or semicommercial scale. It is because the separated from quartz

sand deposit glauconites often need high-cost treatment (i.e. improving their surface properties) in order to use them as high quality sorbents. Therefore, for needs of modification the mineral composition of mixture, that is used in lightweight of aggregate production, only separated from quartz sand deposit glauconite was used (without no surface modification).

The purpose of the presented research is to assess the possibility for the use of spent glauconite, obtained from a wastewater treatment plant, as an additive in the production of lightweight of aggregate. Pickle bath washings from zincing plant „PZL Świdnik” were used for treatment purposes. The resultant waste material in the form of the spent glauconite was built into ceramic sinter matrix (e.g. lightweight of aggregate) through thermal processing.

The outcome of the presented research was management of the spent ion-exchange material and creation of a useful

material characterized by a wide array of applications in construction, environmental engineering, geotechnics and horticulture.

2. GLAUCONITE ADSORBENT OCCURRENCE AND CHARACTERIZATION

Glaucosite is a commonly occurring surface mineral in the Lublin region. It is found mainly in tertiary quartz sand deposits and in which are related to the sedimentation of the Upper Paleogene (Eocene and Oligocene). Quartz-glaucosite sand from the city Nowodwór was used as the initial input material in the research.

The petrographic form of these sediments allow for easy and economically justified separation of the glaucosite, which due to specific magnetic properties is a good source of high glaucosite concentrate. Therefore separated from this sand glaucosite was used to described examinations.

3. METHODS

Glaucosite is a clay mineral which forms four mineralogical variations of very characteristic physical, chemical and surface properties; therefore, a detailed mineralogical examination was performed using diffraction method (XRD) and scanning electron microscope (SEM) which was further supplemented by determination of physical properties, ion exchange capacity as well as texture parameters.

The physical properties of glaucosite were investigated according to EU Standards: EN 933-1, EN 1097-3, ISO/TS 17892.

The mineral composition of glaucosite was determined via the powder X-ray diffraction (XRD) method using Philips X'pert APD diffractometer (with the PW 3020 goniometer), Cu lamp, and graphite monochromator. The analysis was performed within the angle range of 5-65 2 θ . Diffraction data were processed using Philips X'Pert software.

The morphology of glaucosite and lightweight of aggregate were determined using the electron scanning microscope (SEM). The equipment used was a FEI Qanta 250 FEG scanning microscope.

Cation exchange capacity (CEC) of the glaucositic material was determined on the basis of the amount of Ba²⁺ ions saturated in the sample (exchangeable cations were K⁺, Na⁺, Ca²⁺) and desorbed by 1M MgCl₂. This method is recommended by international association AIPEA [16,17].

The specific surface area, pore size and radius dependent distribution was determined on the basis of the shape of nitrogen pairs adsorption/desorption isotherm at -194.85°C temperature using ASAP 2405 Micromeritics analyzer. The previously mentioned glaucosite texture parameters were determined after previous degassing of the sample under strictly controlled conditions at temperature (250°C, during 24 hours) and reduced pressure (10⁻³ hPa).

The chemical composition of glaucosite was determined using Atomic Emission Spectroscopy (ICP), JARRELL ASH Enviro model and Inductively coupled plasma mass spectrometry (ICP/MS), model Parkin Elmer Elan 6000.

The experiment to remove zinc ions from „PZL Świdnik” washings was performed on the glaucosite under dynamic

conditions. The following ion concentrations were found in the examined pickle bath washings: Zn²⁺ = 47.85 mg/dm³, K⁺ = 123.00 mg/dm³, Na⁺ = 10.31 mg/dm³, B⁺ = 3.48 mg/dm³, V²⁺ = 3.47 mg/dm³, Ca²⁺ = 1.00 mg/dm³, Al³⁺ = 0.26 mg/dm³, Mg²⁺ = 0.20 mg/dm³, electrical conductivity 56 mS, pH 2.2.

In order to access the possibility of spent glaucosite practical usage a dynamic sorption experiment was carried out onto pure glaucosite. Next, the pickle bath washings were passed through the glaucosite bed. Obtained in this process spent glaucosite (in various amounts) was added to lightweight of aggregate mixtures.

Clay from „Budy Mszczonowskie” bed was used to produce lightweight of aggregate with an addition of glaucosite. The operated deposit area belongs to Lightweight Aggregates Enterprise „Keramzyt” in Mszczonów. Material collected from the mine was air-dried, milled in a mortar mill and then finely ground with a mortar and pestle to obtain a fraction below 1.0 mm. Next, sets of aggregates having a mass of 150 g each were prepared on a base of clay (marked as M), clay and glaucosite (marked as MGI) as well as clay and glaucosite contaminated with zinc (marked as MGIzn). Aggregate mixtures MGI i MGIzn contained clay and variable amounts (10, 15, 20, 25 weight percent) of the spent glaucosite. Appropriate mass proportions of dry aggregate mixtures were treated with the amount of distilled water necessary to obtain a pliable state. The amount of used water varied between 27-29%.

Handmade sets of aggregate mixtures were formed into cylinders having a diameter and height of 10 mm. The air dried cylinders were then further dried in a lab dryer for 2 hours at a temperature of 105°C.

Lightweight of aggregate's properties depend on the nature of raw material used, firing conditions e.g. atmosphere and the firing temperature.

In the Lightweight Aggregates Enterprise „Keramzyt” raw material, fired in a rotary kiln in an oxidizing atmosphere, is passed through technological zones of different temperatures. A maximum temperature of 1200°C is present in the firing zone. Because of the firing conditions of raw material in the Lightweight Aggregates Enterprise „Keramzyt” the cylinders were fired in a laboratory kiln in an oxidation atmosphere at temperatures 1140°C and 1200°C.

The impact of natural glaucosite and glaucosite contaminated with zinc on temperatures characteristic of lightweight of aggregate was assessed on the basis of experiments conducted on a high-temperature thermovision microscope.

Temperature gain in the high-temperature microscope was found to be up to 1100°C – 30°C/1min and over 1100°C – 10°C/1min. The experiment was performed in an oxidation atmosphere and up to the maximum temperature of the high-temperature microscope - 1500°C.

The samples - raw material mixtures - after being combined with water and squeezed in a hand press (to obtain a cylindrical shape, 3 mm in diameter and 3 mm high) were subjected to thermal processing.

The Maximum Leaching (ML) method was employed in order to determine the degree of leaching of elements from the aggregates. It was chosen because it is simple in use and the reproducibility of results is high. The ML method is applied to access of immobilization level of heavy metals from building materials. It allow to determine maximal leaching of

substances form tested materials at extremely conditions of environment. Besides, essential is to note that granularity of the tested sample should be below 125 μm and the process is conducted at $\text{pH} = 4$. So, this conditions are unfavorable for immobilization of metals (large contact surface of tested sample with solution and acid environment are favorably in leaching of metals) [18]. This method determines the maximum amount of elements leached from the matrix.

Distilled water in the amount of 500 ml, acidified with 1N HNO_3 to $\text{pH} = 4$, was added to 5 grams of ground-up samples which had a fraction below 125 μm . Samples prepared in this way were shaken for 5 hours, and pH of the solutions throughout the process was kept constant by using 1N HNO_3 . The very large liquid to solid ratio ensures that the contaminant release is not constrained by its solubility. After leaching the suspensions were centrifuged. The obtained clear solutions were decanted and the concentration of zinc and the remaining elements were detected with ICP-OES method using a (JOBINYVON U-238) spectrometer. Concentrations of elements found in solutions after leaching are a measure of immobilization stability of the elements in samples.

5. RESULTS

Glauconite used for the experiments had a grain fraction of 0.125-0.5 mm (60% of total mass of glauconite), with specific density of 2.74 g/cm^3 and bulk density of 1.38 g/cm^3 . Filtration coefficient is equal 2.60 $\cdot 10^{-3}$ cm/s which corresponds to the values of filtration coefficient for midgrained soils.

X-ray diffraction features of the examined glauconite (well visible diagnostic reflections, sharp and symmetrical shape of basal reflections, intensity index I₁) revealed that this glauconite represents a variation which has a very well-structured arrangement, of the ISII arrangement packet type with high potassium content and swelling packages in the range of 5 - 15%. This allows for the inclusion of the examined glauconite into a polytype 1M.

The vast majority of glauconite grains have a smooth, very often cracked surface, sometimes filled with a secondary mineral represented by iron oxides.

Irregularly distributed plate-like aggregates are visible in the cracks of the grains, next to which there are micro areas where these plates exhibit an obviously ordered (Fig 1A, B).

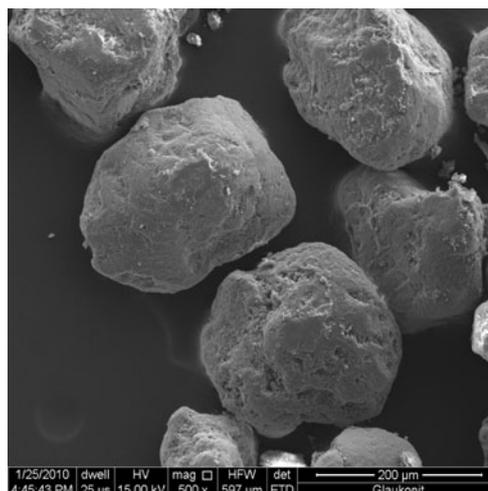


Fig. 1A. Grains of glauconite, SEM zoom 500X.

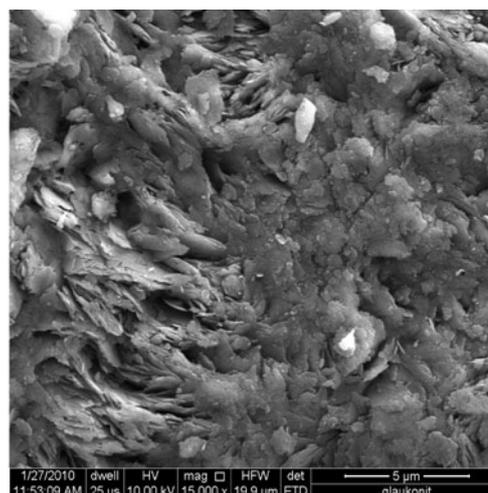


Fig. 1B. Small flakes of glauconite, SEM zoom 15 000X.

TABLE 1: MINOR AND TRACE ELEMENTS OF THE GLAUCONITE (NOWODWÓR) [MG/KG]

Au	Ag	As	Ba	Be	Bi	Br	Cd	Co	Cr
< 5	1.5	17	24	7	2	< 1	0.9	19	206
Sb	Sc	Se	Sr	Ta	Th	U	V	W	Y
1.9	7.9	< 3	23	< 1	1.8	< 0.5	148	< 3	4
Cs	Cu	Hf	Hg	Mo	Ni	Pb	Rb	S	Zn
4	17	1.5	< 1	< 5	55	19	250	0.005	79
Zr	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	
55	1.7	6	< 5	0.5	< 0.1	< 0.5	0.4	0.07	

Ion exchange capacity of the glauconite used for the treatment of pickle bath washings was determined using barium-exchanged method and equaled 17 meq/100g. The BET specific area of the glauconite equaled 58 m²/g.

According to the IUPAC classification, nitrogen's sorption isotherm for the tested material represents a Type II with a hysteresis loop of Type H3. Such an isotherm profile is characteristic of micro- and mesoporous structures, and the hysteresis loop corresponds to the pores of rectangular cross-section with non-uniform size, produced by the plate or lamellar aggregate particles. In the tested glauconite 3 nm pores prevail which is characteristic of mezoporous materials.

Chemical analysis of the tested glauconite from Nowodwór has revealed its main components to be: SiO₂ (49.16-50.52%); Fe₂O₃ (20.01-20.50%), K₂O (8.40-7.66%), Al₂O₃ (5.11-6.04%) i MgO (4.04-4.27%). Worth noticing is the low content of CaO (0.36-0.42%) and Na₂O (0.02-0.08%), which is confirmed by small amounts of swelling packets in the structure of the tested material and its belonging to a well ordered type.

Table 1 presents the concentrations of minor and trace elements in the glauconite from Nowodwór. Rubidium, chromium, vanadium and zinc, zirconium, lead and barium were found to be the predominant elements.

Basic parameters of the ion exchange process are: breakthrough time 840 min, exhaustion time of the glauconite bed 1440 [min], operating exchange capacity 0.129 [mval/cm³], maximum exchange capacity 0.239 [mval/cm³]. Exhaustion of the glauconite's ion exchange properties with respect to zinc ions occurs after 154 units of deposit wastewater volume flows through the deposit.

After treatment of 90 bed volumes of the deposit wastewater, the Zn²⁺ ions pass through the glauconite deposit and the zinc ion concentration in the eluate is equal to the maximum permissible values of metal concentrations in wastewaters allowed to be discharged into waters and soils according to EU Directive 98/83/EC of November 1998.

The result of removing zinc ions from the washings indicate the possibility for the use of glauconite mineral in wastewater pretreatment which in turn allows the wastewater to be discharged into water or soil.

Figure 2 shows fired mixtures of clay and glauconite samples in the amount of 10, 15, 20 and 25 weight percent. For

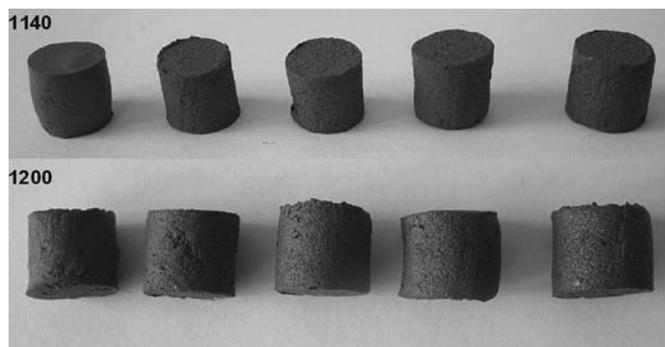


Fig. 2. Lightweight of aggregate obtained at 1140°C and 1200°C temperature (from the left side), purely clay based aggregate, clay + 10 weight % of glauconite, clay + 15 weight % of glauconite, 20 weight % of glauconite and clay + 25% weight % of glauconite.

comparison aggregate on a base of spent glauconite and clay is presented in the figure 3.

A comparison with a purely clay based aggregate was made in order to determine the influence of the addition of natural and zinc contaminated glauconite on the texture of the sinter.

Lightweight of aggregate's pellets were polished and fired at temperatures of 1140°C and 1200°C. Images of the polished pellet samples obtained via scanning electron microscope are presented in figures 4-6.

The texture of clay aggregate is compact and includes a few small pores (figure 4A, B). Pellets of the mixtures modified with the 25% of glauconite (both natural glauconite and contaminated with zinc) fired at 1140°C and 1200°C temperature have a vitrified surface which is a desirable feature for construction aggregate.

Additionally there are numerous pores inside of the pellets, which are slightly bigger than those present in the sinter without glauconite additive, favorably reducing apparent density of the material. Sinters modified with natural and spent glauconite, fired in the higher temperature show a more porous texture.

Values of specific temperatures of clay, mixture with glauconite contaminated with zinc and for mixture with natural glauconite are presented in the figure 7.

The zinc contaminated glauconite introduced into the raw material mixtures caused an increase in temperature at the beginning of the sintering process. Whilst the effect of natural glauconite on the temperature at the beginning of the sintering process was negligible. The values of softening, maximum swelling and flow temperatures of the contaminated glauconite and natural glauconite samples were higher when compared to purely clay samples.

The increase of maximum swelling temperature of contaminated glauconite samples was inversely proportional to the participation of the additive. Such a trend was not observed in samples containing natural glauconite in the aggregate mixture. The maximum swelling temperature in the tested samples containing glauconite ranged from 1352°C (for 10% of natural glauconite) to 1388°C (for 10% of contaminated glauconite).

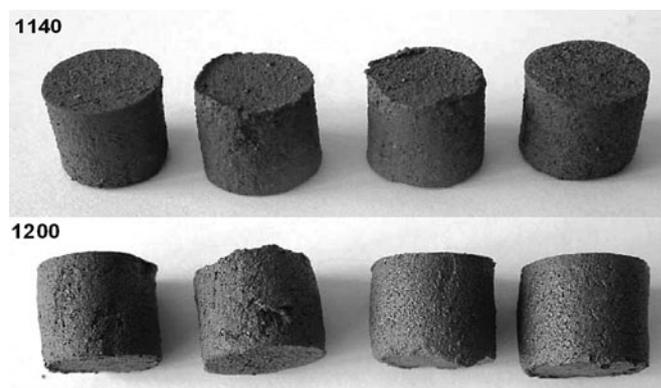


Fig. 3. Lightweight of aggregate fired at 1140°C and 1200°C temperature (from the left side), on a base of clay + 10 weight % of spent glauconite, clay + 15 weight % of spent glauconite, 20 weight % of spent glauconite and clay + 25 weight % of spent glauconite.

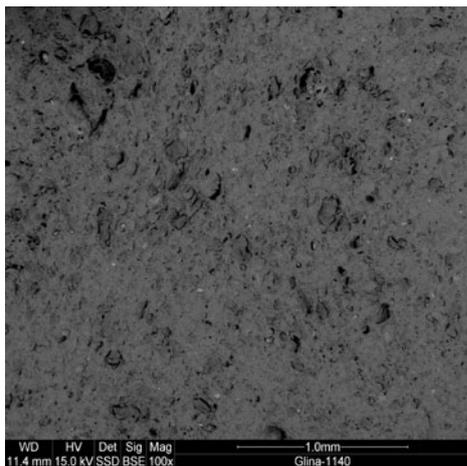


Fig. 4A. Polished pellets sample: clay fired at 1140°C, SEM, zoom. 100X.

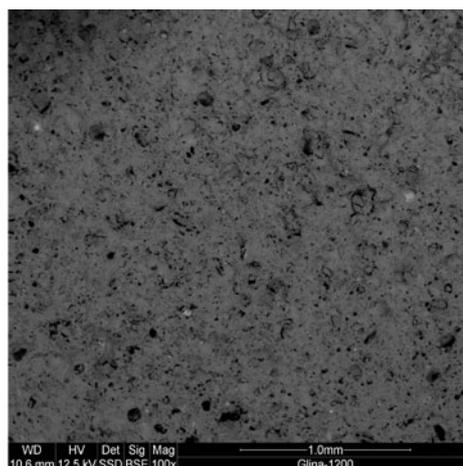


Fig. 4B. Polished pellets sample: clay fired at 1200°C, SEM, zoom. 100X.

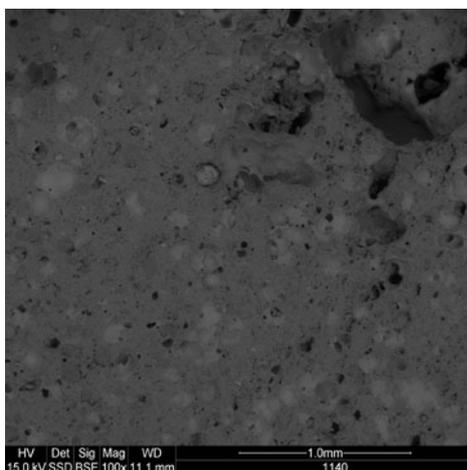


Fig. 5A. Polished pellets sample: clay + 25 weight % of natural glauconite fired at 1140°C, SEM, zoom. 100X.

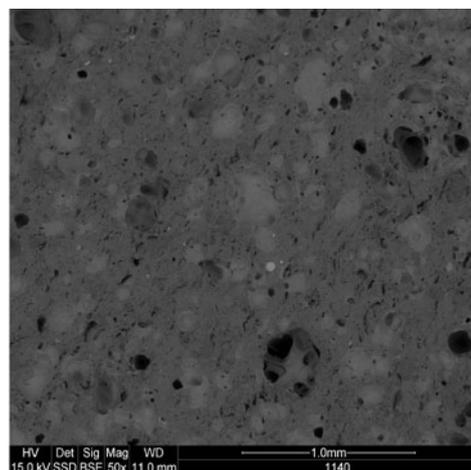


Fig. 5B. Polished pellets sample: clay + 25 weight % of spent glauconite fired at 1140°C, SEM, zoom. 100X.

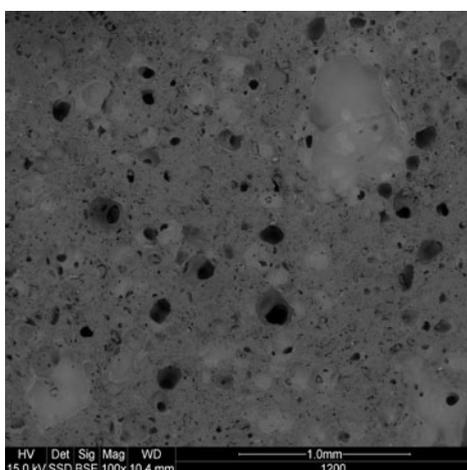


Fig. 6A. Polished pellets sample: clay + 25 weight % of natural glauconite fired at 1200°C, SEM, zoom. 100X.

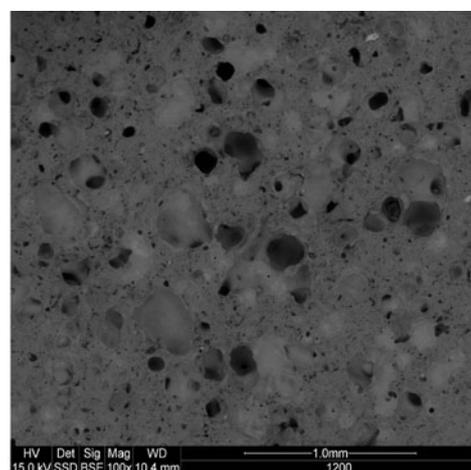


Fig. 6B. Polished pellets sample: clay + 25 weight % of spent glauconite fired at 1200°C, SEM, zoom. 100X.

To meet the conditions required for the usability of the raw material in the production of lightweight of aggregate (e.g. to achieve maximum swelling in temperature not exceeding 1300°C [19], it is necessary to introduce a fluxing agent into the tested mixtures.

An optimal fluxing agent, especially in terms of economic viability as it pertains to lightweight of aggregate production, is one derived from waste material.

The melting temperature increased by 27°C in the 10% contaminated glauconite additive and by 9°C in the sample with 15% of contaminated glauconite additive. The sample with 15% additive of natural glauconite showed a slight increase of its melting temperature. For the remaining mixture samples beneficial lowering of the melting temperature was detected when compared to the clay sample.

The parameter determining suitability of the raw material in the production of lightweight of aggregate is the swelling interval of minimum 50°C, which is the range between softening temperature and maximum swelling temperature [19]. All investigated aggregate mixtures met this important technological criterion. The lowest value of swelling interval of 77°C was observed in the aggregate mixture with 15% additive of natural glauconite, while the highest of 110°C was detected in the mixture with 25 % additive of contaminated glauconite.

The concentrations of elements derived from elution tests performed on selected lightweight of aggregate mixture samples on a base of glauconite and clay, clay and spent glauconite of variable weights, fired at temperatures of 1140°C and 1200°C are shown in the Table 2.

The concentration of zinc in the aqueous leachate, after leaching lightweight of aggregate on a clay and natural glauconite base (10%, 15%, 20%, 25%) and firing at 1140°C, was low and varied from 5.06 to 18.22 µg/dm³ and don't exceed 15% of Zn content. Whilst in the samples fired at the temperature of 1200°C zinc concentration was found to be higher, ranging from 17.58 to 21.34 µg/dm³ and don't exceed 18% of Zn content. Results indicate that the higher the firing temperature, the higher the amount of zinc in the aqueous leachate. These differences are probably the result of the analytical error caused by very low zinc concentrations in the aqueous leachates.

The concentration of zinc detected in the aqueous leachate of the lightweight of aggregate containing clay and spent glauconite, fired at 1140°C temperature ranged from 15.92 µg/dm³ to 30.77 µg/dm³ and don't exceed 3% of initial Zn content, however, in the lightweight of aggregate fired at 1200°C concentrations ranged from 24.11 to 37.13 µg/dm³ and don't exceed 15% of Zn content. The amount of zinc in aqueous leachate is also dependent on its presence in the clay used in the production of the aggregate.

TABLE 2: CONCENTRATIONS OF ELEMENTS LEACHED FROM THE LIGHTWEIGHT OF AGGREGATE AGGREGATES, FIRED AT 1140°C AND 1200°C.

Compositions of raw material mixtures	Zn	Zn	Al	Ba	Bi	Ca	Cu	Fe	K	Mg	Mn	Na	Pb
	µg/dm ³	%	mg/dm ³										
M (1140)	17.34	39.6	1.11	0.05	0.01	1.42	0.01	0.26	1.07	0.27	0.01	0.12	0.01
M (1200)	21.50	50.0	1.76	0.05	0.01	1.39	0.01	0.38	1.49	0.61	0.02	0.19	0.02
M _{Gl} (1140) ₁₀	18.22	15.4	2.15	0.08	0.03	1.17	0.01	0.50	2.85	0.56	0.01	0.28	0.04
M _{Gl} (1200) ₁₀	20.84	17.5	3.71	0.08	0.02	1.47	0.01	0.86	3.97	1.23	0.02	0.40	0.04
M _{Gl} (1140) ₁₅	15.66	10.1	4.42	0.16	0.01	2.08	0.01	1.08	7.89	1.60	0.03	0.72	0.03
M _{Gl} (1200) ₁₅	20.00	12.9	4.14	0.18	0.02	1.68	0.01	0.50	6.20	1.66	0.03	0.58	0.05
M _{Gl} (1140) ₂₀	5.06	2.6	2.17	0.09	0.02	1.25	0.01	0.17	4.74	0.74	0.02	0.32	0.01
M _{Gl} (1200) ₂₀	31.53	11.2	3.07	0.07	0.02	1.48	0.01	0.39	4.88	1.27	0.02	0.66	0.03
M _{Gl} (1140) ₂₅	12.37	5.4	2.82	0.07	0.01	1.26	0.01	0.50	5.62	1.07	0.02	0.33	0.02
M _{Gl} (1200) ₂₅	17.58	7.7	3.72	0.06	0.02	1.30	0.01	1.46	5.72	1.39	0.02	0.33	0.03
M _{GlZn} (1140) ₁₀	24.53	3.0	4.18	0.19	0.02	2.56	0.01	0.65	6.82	1.45	0.03	0.78	0.03
M _{GlZn} (1200) ₁₀	24.11	3.0	3.18	0.09	0.02	1.32	0.01	0.42	4.16	1.23	0.02	0.49	0.03
M _{GlZn} (1140) ₁₅	29.49	2.4	4.20	0.14	0.02	2.16	0.01	0.62	8.41	1.58	0.03	0.85	0.04
M _{GlZn} (1200) ₁₅	36.13	3.1	3.45	0.07	0.02	1.36	0.01	0.67	4.90	1.30	0.02	0.53	0.04
M _{GlZn} (1140) ₂₀	15.92	1.0	2.16	0.11	0.03	1.12	0.01	0.46	4.00	0.71	0.01	0.39	0.03
M _{GlZn} (1200) ₂₀	37.13	2.4	2.93	0.06	0.02	1.29	0.01	0.67	5.75	1.33	0.02	0.45	0.03
M _{GlZn} (1140) ₂₅	30.77	1.6	2.52	0.10	0.02	1.26	0.01	0.58	6.03	1.00	0.02	0.42	0.04
M _{GlZn} (1200) ₂₅	34.89	1.8	2.74	0.05	0.02	1.08	0.01	0.96	4.99	1.00	0.02	0.29	0.04

Explanations: M_{GlZn} - clay + spent glauconite, M_{Gl} - clay + natural glauconite, 10; 15; 20; 25% weight percent of natural or spent glauconite

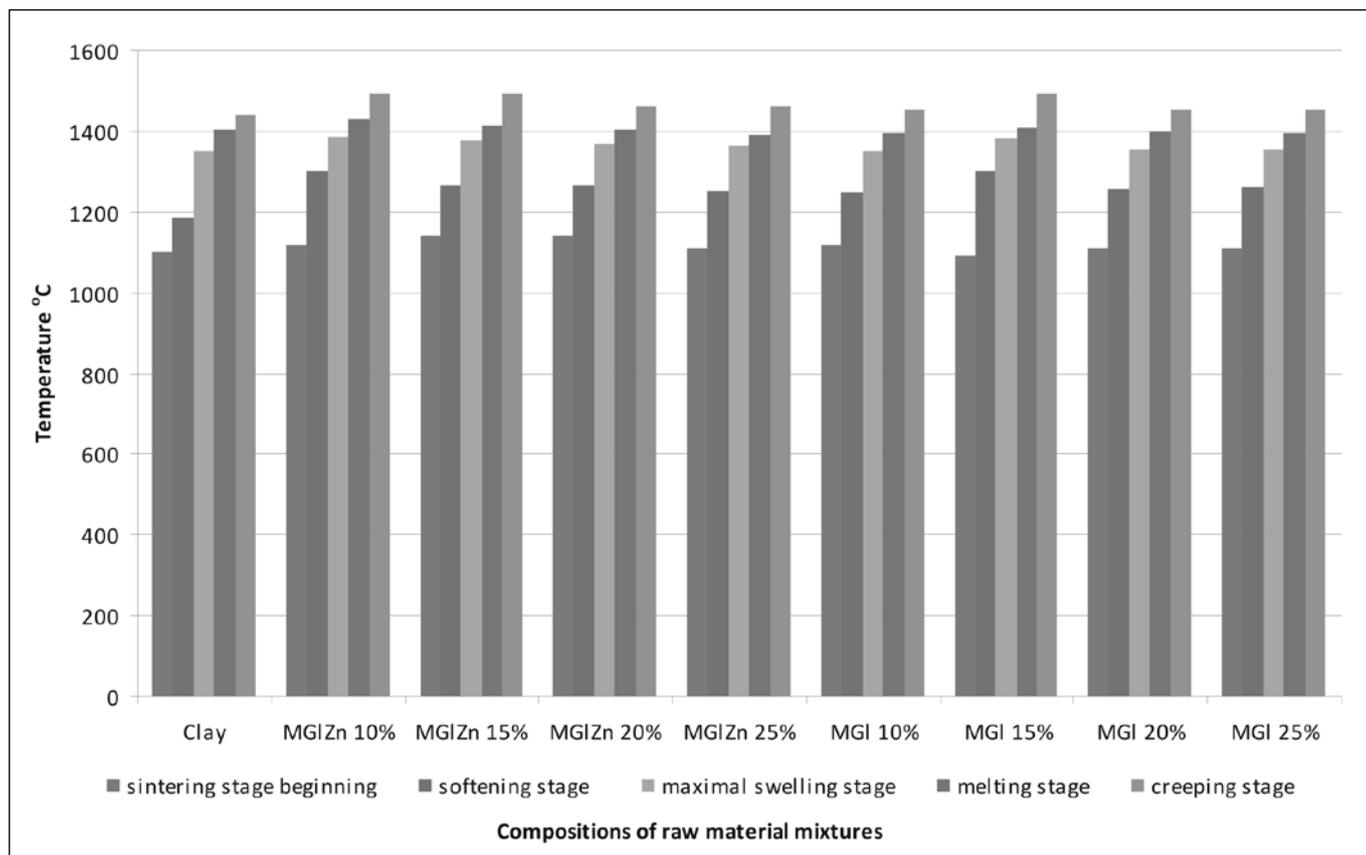


Fig. 7. Specific temperatures of clay and mixtures modified by natural glauconite, zinc contaminated glauconite.

Concentrations of zinc and other elements detected in the leachates are much lower than the concentrations allowed to be discharge into the quality water intended for human consumption (EU Directive 98/83/EC of November 1998).

Variable quantities (10, 15, 20 and 25%) of spent glauconite present in the aggregate do not cause significant changes in concentrations of the leached zinc and remain at similar levels, which is an indication that the spent mineral aggregates in the matrix have been highly stabilized.

Results of average zinc ions concentration (that come from leaching of aggregate), were subjected NIR tests with level of significance $\alpha = 0,05$. It revealed that there are exists statistical differences between average concentrations of zinc ions for different firing temperatures (1140 and 1200°C) and for content of spent glauconite and clays in aggregates (this is evidence of p value ranges from $1,29 \cdot 10^{-3}$ do $9,19 \cdot 10^{-16}$). The least essential differences were in comparison with average concentration of leached zinc ions from aggregate with 10% wt. and 20% wt. of glauconites fired at 1140 and 1200°C, respectively.

Average value of zinc ions leached from aggregates containing 20 and 25% wt. of pure glauconite, fired at temperature 1140°C, and leached from aggregates containing pure glauconite at amount of 15, 20 25% wt., fired at temperature 1200°C in relation to remaining aggregates has shown the least essential differences (p ranges from $1,08 \cdot 10^{-3}$ do $8,75 \cdot 10^{-5}$).

6. CONCLUSIONS

- The obtained results indicate that applying glauconite to remove zinc ions from wastewaters is feasible.
- The use of spent mineral as an additive to lightweight of aggregate avoids generating hazardous wastes. Chemical elements, including heavy metals, become built into the texture of the sinter.
- Swelling temperatures of the tested aggregate samples which are higher than the required 1300°C do not preclude usage of the spent mineral in production of lightweight of aggregate. Thermal swelling of the aggregate is a comprehensive process dependant on several factors therefore requiring further investigation.
- Addition of spent glauconite into the lightweight of aggregate mixture results in an increase of the porosity of lightweight of aggregate.

REFERENCES

1. Spoljaric N., Crawford W.A.: Removal of contaminants from landfill leachates by filtration through glauconitic greensand, *Environmental Geology*, 2, 359-363, 1979.
2. Hao O.J., Tsai C.M., Huang C.P.: The removal of metals and ammonium by natural glauconite, *Environmental International*, vol.13, no 2, 203-212, 1987.
3. Smith E. H., Lu W., Vengris T., Binkiene R.: Sorption of heavy metals Lithuanian glauconite, *Water Research* 12, 288-32892, 1996.
4. Smith P.R.J.: The use of a glauconitic clay to remove metals from solution, Report by Aquatonics Ltd. Available from Aquatonics Ltd., 2000a.
5. Smith P.R.J.: Use of a glauconitic clay to remove copper from effluents produced during manufacture of printed circuit boards, Report by Aquatonics Ltd. Available from Aquatonic Ltd, 2000b.
6. Srasra E., Trabelsi – Ayedi M.: Textural properties of acid activated glauconite, *Applied Clay Science*, vol. 17, 71-84, 2000.
7. Ringqvist L., Holmgren A., Öborn I.: Poorly humified peat as adsorbent for metals in wastewater, *Water Research* 36, 2394-2404, 2002.
8. Franus W., Klinik J., Franus M.: Mineralogical characteristic and textural properties of acid - activated glauconite, *Mineralogia Polonica*, vol. 35/2, 53-62, 2004.
9. Franus M.: Removal of heavy metals on glauconite and glauconite-quartz mixture beds, *Polish Journal of Environmental Studies*; vol. 16, No.2A, Part III, 534-538, 2007.
10. Rengaraj S., Yeon K. H., Moon S. H.: Removal of chromium from water and wastewater by ion exchange resins, *Journal of Hazardous Materials B87*, 273-287, 2001.
11. Inglezakis V. J., Loizidou M. D., Grigoropoulou H. P.: Ion exchange of Pb^{2+} , Cu^{2+} , Fe^{2+} , and Cr^{3+} on natural clinoptilolite selectivity determination and influence of acidit on metal uptake, *Journal of Colloid and Interface Science*, 261, 49-54, 2003.
12. Bosco S. M. Jimenez R. S., Carvalho W. A.: Removal of toxic metals from wastewater by Brazilian natural scolecite, *Journal of Colloid and Interface Science* 281, 424-431, 2005.
13. Medvidović Vukojević N., Perić J., Trgo M.: Column performance in lead removal from aqueous solutions by fixed bed of natural zeolite – clinoptilolite, *Separation and Purification Technology*, vol. 49, 237-244, 2006.
14. Dohrman R.: Cation exchange capacity methodology I: An efficient model for the detection of incorrect cation exchange capacity an exchangeable cation results, *Applied Clay Science* 34, 31-37, 2006.
15. Latosińska J., Żygadło M.: Effect of sewage sludge addition on porosity of Lightweight Expanded Clay Aggregate (LECA) and level of heavy metals leaching from ceramic matrix, *Environmental Protection Engineering Journal*, 2, 189-196, 2009.
16. Gillman P., A proposed method for measurement of exchange properties of highly weathered soils. *Australian Journal of Soil Research*. 17, 129-139, 1979.
17. Derkowski A., Franus W., Waniak-Nowicka H., Czimerová A., Textural properties vs. CEC and EGME retention of Na-X zeolite prepared from fly ash at room temperature. *International Journal Mineral Processing* 82, 57-68, 2007.
18. Rankers R. H., Hohberg I.: Leaching tests for concrete containing fly ash – evaluation and mechanism, In: Goumans J.J.J.M., van der Sloot H.A., Aalbers Th.G. (Ed.) *Waste Materials in Construction*, Amsterdam, Elsevier, 275-282, 1991.
19. Galos K., Wyszomirski P.: *Przetwórstwo termiczne surowców ilastych, Surowce mineralne Polski, Surowce skalne. Surowce ilaste*, [ed.] Ney R., IGSMiE PAN, Kraków, 307-326, 2004.

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