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INFLUENCE OF CATALYST WASTE ON CERAMICS AND EXPANDED CLAY LIGHTWEIGHT CONCRETE PROPERTIES

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ABSTRACT

Influence of the use of catalytic cracking catalyst waste on the properties of building ceramics and expanded clay concrete (density, compressive strength, water absorption, porosity) is analysed in the paper. The work contains description of raw materials of building ceramics and expanded clay concrete and the catalyst waste characteristics. The physical and mechanical properties of building ceramics and expanded clay concrete samples are also presented. Phase analysis of burned ceramic samples and expanded clay concrete was carried out by the method of X-ray diffraction. Technogenic raw material – used catalyst may be utilised in the building ceramics and expanded clay lightweight concrete production have been determined. About 10% of milled catalyst waste may be applied to the formation mix.

1. Introduction

In recent years, there has been an increasing interest in sustainable development of waste-free manufacture. Different wastes might be used in the production of building ceramics and expanded clay lightweight concrete and may even improve the properties of ceramic products.

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Lithuanian oil refinery company “ORLEN Lietuva” utilises more than 40 types of various catalysts. Two types of catalyst waste materials are produced during the processing: coarse-grained and fine-grained. In recent years the scientists have carried out widely the research on the secondary usage of catalyst waste materials. Main components of the catalyst waste materials are SiO_2 and Al_2O_3.

Oil refinery is an important and strategic branch of industry. The oil refineries alone satisfy 42% of EU energy needs and produce 95% of fuel necessary for transport, yet processing huge amounts of crude oil the by-products – technogenic raw materials appear, which are formed during the manufacture of the main production. These raw materials are ranked as a factor increasing emission of environmental pollution [1]. Currently oil refineries mostly produce mud and the used chemical materials: catalysts, acids, amines, etc. According to the waste record data, around 130 thousand tons of dangerous waste pile in Lithuania per year [2]. Special attention has been recently devoted to the process of waste minimization, pollution prevention and self-sustainable development as applied to the materials field [3 – 5]. The used catalyst from catalyst cracking reactor of “ORLEN Lietuva” is used in the production of heat resistant concrete and is widely analysed in the works of Lithuanian researchers [2, 6 – 9]. Investigations on oil refinery catalyst wastes and their application possibilities in construction industry in the similar direction are also performed in the other countries [10, 11].

The oil refinery wastes in Europe are used in the production of cement clinker and asphalt concrete. It is determined that catalyst technogenic materials may be utilised in building ceramics. However, applying these materials to formation mix affects the burning parameters; the materials in catalyst increase the burning temperature of the ceramic body [12].

The authors [13, 14] state, that mixes of clay and oil refinery waste may be use in the manufacture of the main ceramic products (facade bricks, blocks, tiles). However, the densification of products and the processes taking part during sintering were not fully analysed in these works.

In the work of researchers [15] the properties of products are analysed changing the quantity of oil waste from 5% to 20% and the highest burning temperature from 750 °C to 1150 °C; also, the important morphological changes in ceramic bodies during burning are defined. It is determined that with the most optimal amount of waste – 5%, the subsequent increase in quantity influences the compressive strength of products negatively.

The wastes from oil industry are designated as potential additives for concrete [16] because they are composed of silicon dioxide and aluminium oxide, and act as pozzolans [17 – 19]. During our previous research [16], it was found that when the catalyst waste (15 % comparing to the cement mass) from the reactor of catalytic cracking is used for the lightweight concrete, the density of the analysed expanded clay lightweight concrete and compressive strength (even for the larger water/cement ratio) increase, more heat is dissipated during the hydration of cement and this exothermic effect occurs several hours earlier.

After the reuse of catalyst waste, it has been determined [20], that it can replace 15 – 20% amount of binding material or 10% of fine fillers without worsening the qualitative properties of mortar. Due to special chemical composition and convenient characteristics, the catalyst waste may be used in the manufacture of fire resistant [21 – 22] and ceramic products [23 – 25]. Moreover, the waste is also suitable as a filler in making asphalt concrete or as a pozzolanic component in Portland cement [26]. It has been defined that about 10% of milled catalyst might be applied to a formation mix; larger amount of the waste (20%) has negative influence on the physical-mechanical properties of ceramic body, even when firing the ceramic body at the highest firing temperature [27].

During the analysis of the expanded clay lightweight concrete, where the fractions of coarse aggregates were 5, 15 and 25 mm, scientists [28] have estimated that the highest compressive strength was reached after 28 days of hardening of 15 mm fraction expanded clay. These scientists state that the strength of the concrete with the lightweight aggregates depends on the strength of the utilised light-weight aggregates and on the strength of hardened cement paste.

Scientists [29] who investigated the construction mixtures and grouts, have found that mixture, with water/cement ratio of 0,25 and with 15% of catalyst waste material, reached the maximal compressive strength of 92,3 MPa.

The aim of the work is to perform the analysis of used catalyst waste from “ORLEN Lietuva”, to evaluate the catalysts waste influence on physical-mechanical and structural properties of ceramic body and expanded clay lightweight concrete.

2. Methods and Materials

Ceramic samples with dimensions (70×70×70) mm were shaped manually. Compositions of formation mixes according to weight are shown in Table 1. The composition of formation mixes (ceramic and expanded clay lightweight concrete samples) was chosen according to performed results of previous experiments and generally used by other researchers amount of waste. The part of the research data is published in [30].

Table 1. Composition of formation mixes

No of mix	Composition of formation mixes, wt. %							Maximum firing temperature, °C
	Clay A	Clay B	Sand	Milled glass (S)	Catalyst1 (K1)	Catalyst2 (K2)	Crusched bricks	
C1	75	0	5	0	20	0	0	1050
								1080
C2	75	0	5	20	0	0	0	1050
								1080
C3	75	0	5	10	10	0	0	1050
								1080
C4	75	0	5	5	15	0	0	1050
								1080
C5	75	0	5	15	5	0	0	1050
								1080
C6	60	20	15	0	0	0	5	1050
								1100
C7	0	80	10	0	0	5	5	1050
								1100
C8	65	15	10	0	0	10	0	1050
								1100
C9	60	10	5	0	0	20	5	1050
								1100

Compositions of formation mixtures of the samples of expanded clay lightweight concrete, when catalyst waste is used, are provided in Table 2. The part of binding material in expanded clay lightweight concrete mixtures is replaced with K1 additive.

Table 2. Compositions of expanded clay lightweight concrete mixtures

Marking of mix	Amounts of materials for 1 m^3 of concrete mixture, kg					
	Catalyst1 (K1), %	Portland cement	Ceramsite sand 2/4	Sand 0/4	Water	Catalyst1 (K1)
K0	0	427	312	648	221	–
K1	3	413	311	644	220	12
K2	5	410	315	653	223	21
K3	10	380	309	640	219	42
K4	15	379	325	675	230	66
K5	20	342	312	646	221	84

To determine the properties of expanded clay lightweight concrete, cubes with the dimensions of 100×100×100 mm were formed. The following raw materials were used: Portland-composite limestone cement CEM II/A-L 42,5 N (which satisfies requirements of the LST EN 197-1 standard), natural sand (the maximum particle size 4 mm), ceramsite sand (fraction 2/4), and catalyst (K1) waste. Up to 20% of cement was replaced with catalyst waste obtained from catalyst cracking reactor. The samples of expanded clay lightweight concrete were made and hardened according to the standard LST EN 12390-2.

Phase analysis of burned ceramic samples was carried out by the method of X-ray diffraction. The diffraction meter DRON-7 with Cu anti-cathode and Ni filter / Fe anti-cathode and Mn filter was used when U = 30 kV, Ia = 8 mA and rotation speed of the sample was $1^0 \mathrm{min}^{-1}$. X-ray diffraction pattern was registered on paper by means of typed and decoded comparing with the data of PDC catalogue and research literature [31].

Also, the fusible devonian clay – A (Lithuania) was selected for the research (Clay A). According to the chemical composition, the clay A is semiacid, because the quantity of Al_2O_3 in the heated clay is 15,8%; the clay belongs to the group with a big amount of colorific oxides as 6,42% Fe_2O_3, has low dispersion, is impured by coarse carbonaceous inserts ≥ 3%, has lot of sand fraction, the amount of free quartz ranges 30 – 60%.

Table 3. Chemical compositions of the clay

Chemical composition, %	Raw material	
	Clay A	Clay B
SiO_2	66,33	47,6
Al_2O_3+TiO_2	15,8	17,79
Fe_2O_3	6,42	7,66
CaO	1,8	6,27
MgO	2,72	3,59
MnO	–	0,09
K_2O	1,63	4,49
Na_2O	–	0,55
L.o.l.	5,3	11,55

The fusible hydro – micous clay was selected for investigation (clay B). Granulometric composition of this clay: amount of sand particles > 0,05 mm is from 0,09% to 0,77% amount of dust particles (0,05 – 0,005) mm is from 9,26% to 21,39%, and amount of clay particles < 0,005 mm fluctuates from 72,11% to 96,04%. Chemical compositions of clays are presented in the Table 3.

Chemical composition of unburnt operated catalyst is presented in Table 4.

Table 4. Chemical compositions of the catalyst

Chemical composition, %	Catalyst1 (K1)	Catalyst2 (K2)
SiO_2	55,15	–
Al_2O_3	40,94	68,85 – 85,25
Fe_2O_3	0,90	–
TiO_2	1,48	–
NiO	–	2 – 4
MoO_3	–	10 – 13
P_2O_5	0,11	2 – 6
ZnO_2	–	0,1 – 4
Na_2O	–	0,15
Rare earth element oxides	1,41	0,5 – 4

Bulk density of the catalyst ranges from 0,80 g/cm^3 to 1 g/cm^3; diameter of granules 50 µm – 1,5 mm. The microstructural analysis of catalyst (K1) waste was performed by microscope Carl Zeis Evo LS. Fig. 1 shows a scanning electron micrograph of catalyst waste, which indicates that catalyst particles are spherical.

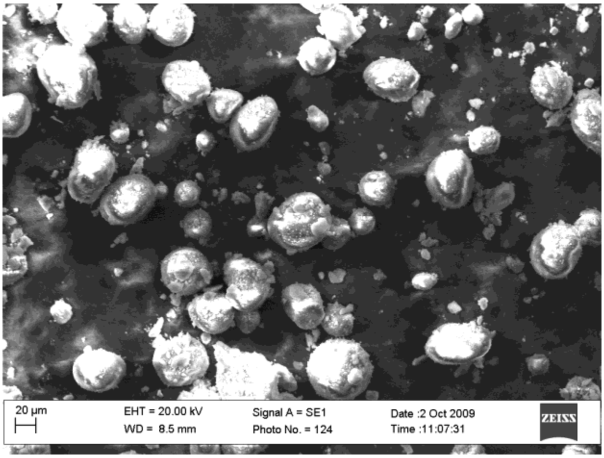

Figure 1. Microstructure of the waste catalyst (K1) grains

The size of milled glass particles varies from 0,03 µm to 63 µm. For the preparation of ceramic samples, usual sand with the fraction of 0/1 was used.

The chemical and mineralogical compositions of Portland cement, which were determined by JSC "Akmenės cementas", are presented in Table 5.

Table 6. Chemical and mineral compositions of Portland limestone cement

CEM II/A-L 42,5 N	
Determined parameter	Amount, wt.%
SiO_2	20,61
Al_2O_3	5,45
Fe_2O_3	3,36
CaO	63,42
MgO	3,84
SO_3^{2-}	0,80
Other	2,18
Non-soluble particles	0,34
C_3S	57,26
C_2S	15,41
C_3A	8,68
C_4AF	10,15
Other	8,50

Chemical compositions of the main raw material were determined by the classical methods of chemical analysis for silicate materials. Physical and mechanical properties of burned ceramic samples were defined according to LST EN 772-1, net dry density – LST EN 772-13, water absorption – EN 772-21.

The samples made of the analysed raw materials were dried to a constant mass in the electric stove under temperature from 100 °C to 110 °C. Dried samples were burned in the electric stove with automatic regulator SNOL – 30/1300 with accuracy of ± 1 °C. The sample burned temperature was 1050 °C, 1080 °C, 1100 °C. The burning demotion was 40 h, and exposure to the highest burning temperature was 3 – 4 h.

The density of the hardened expanded clay lightweight concrete was determined according to the standard LST EN 12390-7, the compressive strength – LST EN 12390-3, and the water absorption – LST 1428.18.

3. Experimental Results and Analysis

The investigation results were divided into two groups: ceramics and expanded clay lightweight concrete.

3.1. Investigation Results for Ceramics

First of all, the XRD analysis of samples was performed. The X-ray diffractograms for the most characteristic batches (containing 20% of catalyst waste in one case and containing 20% of milled glass in the other case) are presented in Fig. 2 and 3.

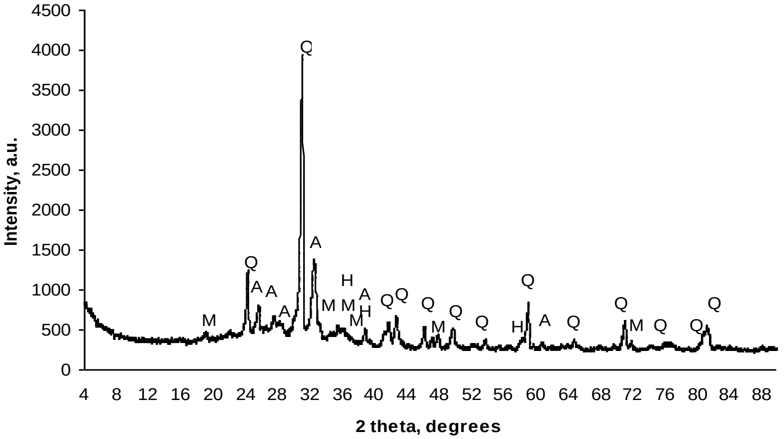

Figure 2. XRD of sample containing 20% of catalyst waste (A – anorthite, Q – quartz, H – haematite, M – mullite)

Ceramic body with 20% of catalyst waste contains the following minerals: A anorthite, Q quartz, H haematite, M mullite.

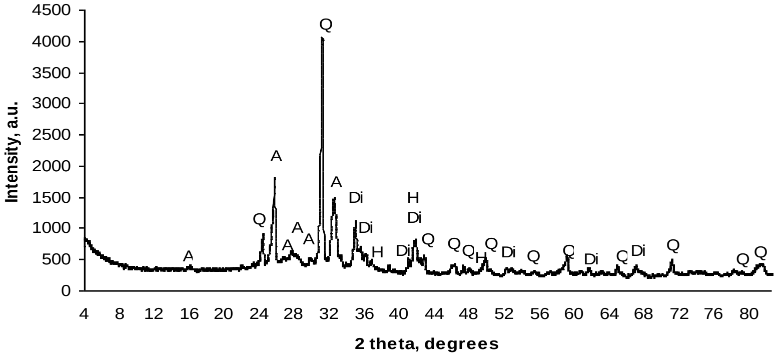

Figure 3. XRD of sample containing 20% of milled glass

Ceramic body with 20% of milled glass additive contains the following minerals: A anorthite, Q quartz, H haematite, Di diopside. As could be seen from Fig. 2 and 3, the main difference of XRD is the different mineral formed: mullite (when catalyst waste is used), and diopside (when glass waste is used).

The sample No.C6 X-ray diffraction patterns identified substances are: quartz – Q, anorthite – A, hematite – He, schpinell – Sp. The main minerals from the X-ray analysis of the 7th ceramic body burned at a temperature of 1100 °C are: quartz, haematite, comparing to the 6th ceramic body the amount of anorthite increases, the peaks of diopside and corundum appear. The X-ray of the 9th ceramic body with the maximum additive of milled catalyst – 20% has shown that besides the main minerals – quartz, haematite and schpinnell, also powellite and corundum appears whose peaks are more intensive than in the 7th ceramic body with non-milled 5% catalyst additive powellite forms during reaction of calcium oxides existing in clay, calcium oxides appearing in the catalyst after use in catalyst cracking reactor and the molybdenum oxide in the catalyst. The X-ray of the 8th ceramic body is similar to the X-ray of the 9th one, yet the intensities of corundum and powellite peaks are smaller, this may be explained by the twice smaller amount of catalyst in the formation mix. The anorthite peaks in this ceramic body remain unchanged as well as in the 9th.

Dependence of building ceramics density, compressive strength, water absorption after 72 hours and reserve of porous volume on formation mix and temperature are presented in the Fig. 4, 5, 6 and 7.

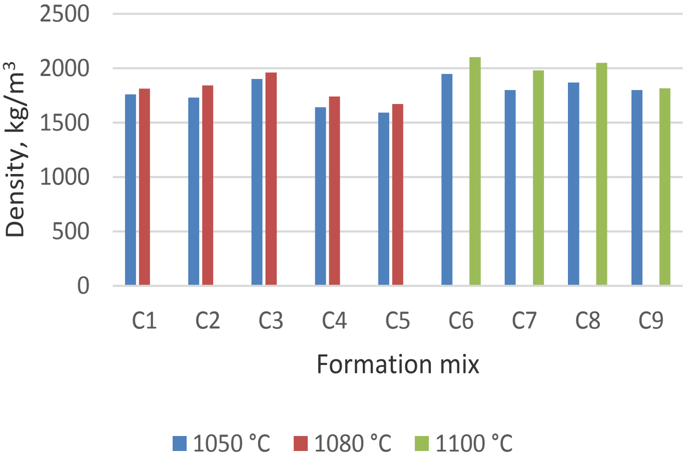

Figure 4. The dependence of ceramics' density on the composition and temperature

As shown in Fig. 4, firing samples at higher temperature leads to higher density. In general, it is possible to state that glass additive increases density, while catalyst waste decreases it. However, the largest density of samples is obtained for formation mixes with 10% of each waste. Burning the ceramic body without the additive of catalyst already at the temperature of 1080 °C and 1100 °C, the samples are obtained with the water absorption parameter less than 4% (Fig. 5; C1, C6), density exceeding 2000 kg/m^3 (C6). However, the compressive strength of these samples is not sufficient ($R_{gn} = 19{,}88$ MPa, Fig. 6) for the samples to be assigned as the sintered ceramic products. Applying milled catalyst additives to formation mix and burning them at different burning temperatures, the water absorptions increase, compressive strengths and reserves of porous volume decrease, only the density and the reserve of porous volume of the ceramic body with 10% of catalyst additive burned at the highest burning temperature are bigger than those of the control one C6.

Water absorption of the C7 ceramic body, burned at the highest burning temperature, is the smallest of the all investigated formation mixes, and the reserve of porous volume, indicating the potential increase in service frost resistance, is the biggest one, the compressive strength increases as well. This ceramic body, after burning at the highest burning temperature, is deep-brown, yet the catalyst does not fully fuse in it, only the catalyst surface slightly fused reacts with the other components of the mix.

As can be seen from Fig. 5, catalyst waste increases water absorption, while glass waste decreases it. The milled glass melts at high temperatures; hard phase sintering takes place based on a liquid-phase. The motive power of this sintering is the surface strain of a melt, which causes negative pressure in a closed pore. Under the negative pressure, the pores of ceramic material are filled with melt and the grains approach each other. The more liquid phase form, the finer is the glass, and the more intensive diffusion process in a sample persists. Due this process, the material grains regroup, the numbers of open pores with irregular shape diminish, the closer, smaller and more regular shape pores appear. As a result, water absorption decreases and density of products rises.

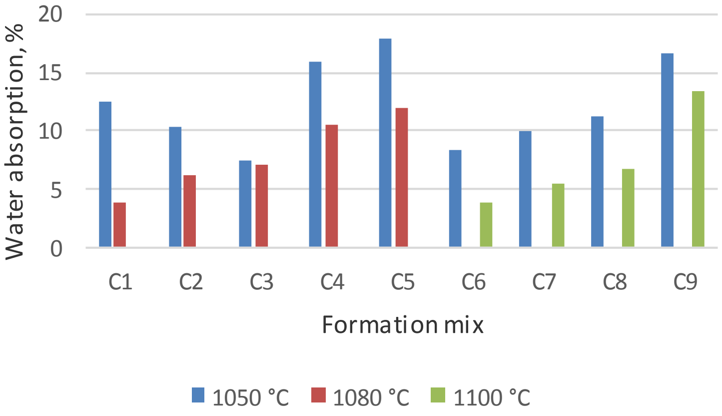

Figure 5. The dependence of ceramics' water absorption on the composition and temperature

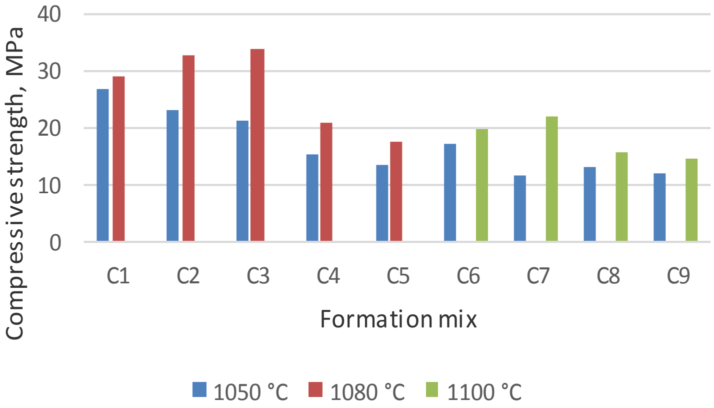

Figure 6. The dependence of ceramics' compressive strength on the composition and temperature

The greatest compressive strength is obtained for samples with 10% of milled glass and catalyst waste (C3) after burning them at temperature of 1080 ^{o}C. Similar compressive strength, i.e. 33 MPa, is obtained when the sole milled glass waste is used. It can be clearly seen from the results that glass increases compressive strength of ceramics samples, while catalyst waste decreases it. At higher temperature, milled glass waste melts, accelerates the sintering process and fills up the pores. Samples become stronger and more resistant to frost.

One of the indicators allowing dealing on frost resistance of ceramics is reserve of porous volume. This indicator shows the percentage amount of pores, which make water difficult to get in, and water in such pores does not freeze. The results of reserve of porous volume of ceramics are presented in Fig. 7.

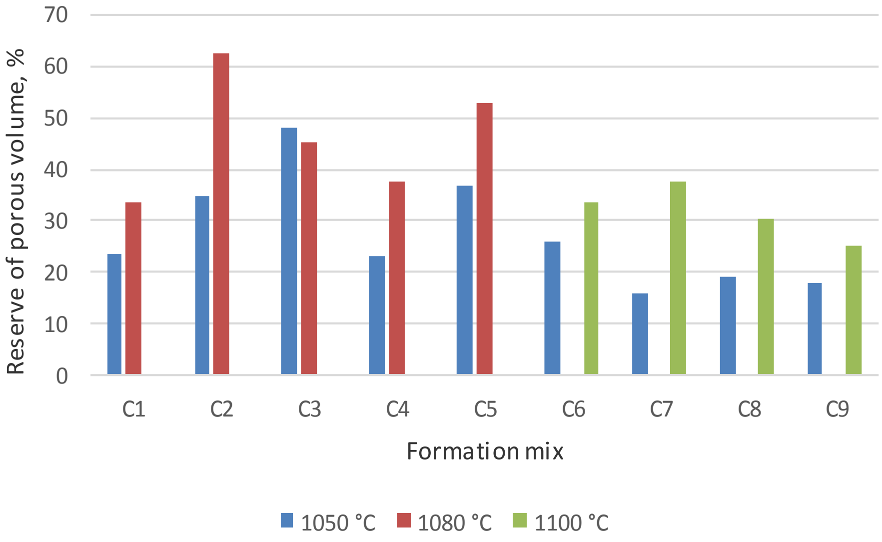

Figure 7. The dependence of ceramics' reserve of porous volume on the composition and temperature

The results in Fig. 7 show the appearance of more closed pores when samples are burnt at higher temperature. The greatest reserve of porous volume is obtained for samples with additionally added milled glass waste.

As can be seen from the discussed results, catalyst waste has a tendency to reduce the density, compressive strength and reserve of porous volume as well as increase water absorption of ceramics. However, using 10% of both, catalyst waste and milled glass waste, the density and compressive strength of ceramics may be increased.

3.2. Investigation Results for Expanded Clay Lightweight Concrete

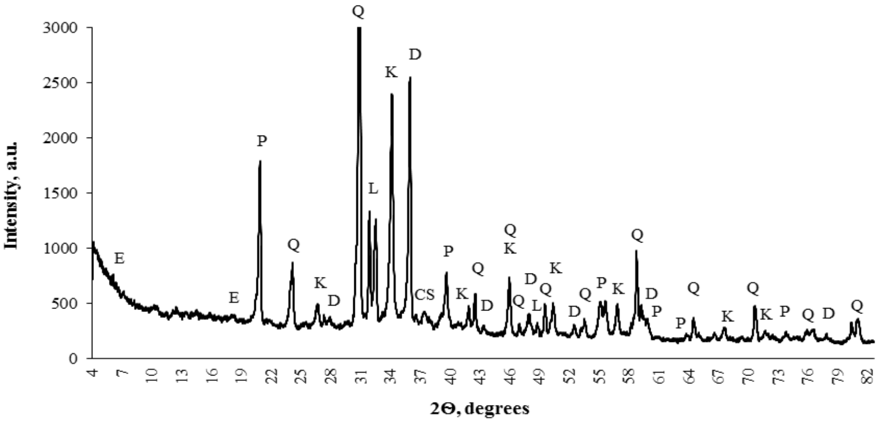

Figure 8. X-ray pattern of the grout part with 3% of catalyst waste of expanded clay lightweight concrete K1 samples: E – ettringite; P – portlandite; Q – silica; K – calcite; D – dolomite; L – feldspars; CS – alite (C_3S)

The work also analyzes X-ray diffraction data of expanded clay lightweight concrete samples which have been hardened for 28 days. The mortar of samples without expanded clay granules is tested. After conducting the X-ray diffraction analysis of mortar in samples K1 (Fig. 8) and K2, the following minerals are determined: ettringite, portlandite, quartz, calcite, dolomite and feldspars. Furthermore, diffraction peaks of non-hydrated alite (C_3S) are identified in 28 days hardened samples K1 and K2, and they are characteristic of spaces *d*, which are, respectively, 0,283 nm, 0,277 nm and 0,278 nm, 0,274 nm. The obtained results allow the conclusion that this mineral does not fully hydrate within 28 days in water. From the data in X-ray diffraction curves, it is observed that expanded clay lightweight concrete with 3% and 5% of catalyst waste has ettringite.

X-ray diffraction analysis of mortar in expanded clay lightweight concrete (Fig. 9) shows that the mixture K4 with 15% of waste as well as sample K3 with 10% of catalyst additive consist of the same minerals: portlandite P, quartz Q, calcite K, dolomite D, feldspars L. However, there are crystals of non-hydrated C_3S minerals, and it is confirmed by diffraction peaks which are 0,278 nm and 0,273 nm. There is gypsum characterising diffraction peak (0,764 nm) as well. The formation of exactly these minerals explains the reduction of compressive strength values for samples K4 compared to samples K3.

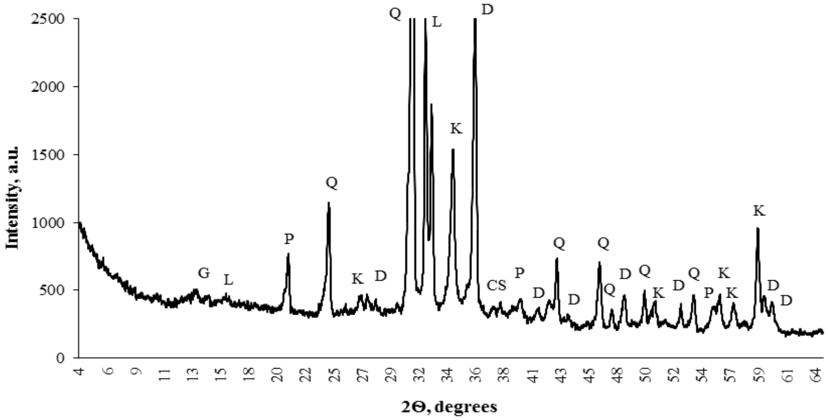

Figure 9. X-ray pattern of the grout part with 15% of catalyst waste of expanded clay lightweight concrete K4 samples: G – gypsum; P – portlandite; Q – silica; K – calcite; D – dolomite; L – feldspars; CS – alite (C_3S)

Expanded clay lightweight concrete with different densities and compressive strength is obtained under different amounts of catalyst waste.

The research results show (Fig. 10) that different amounts of catalyst additive in expanded clay lightweight concrete allow obtaining samples with density ranging from 1371 kg/m^3 to 1445 kg/m^3. Compared to control samples, the density is increased by 4,2% when 15% of catalyst waste is added into the mixture.

Water absorption values (Fig. 11) of selected expanded clay lightweight concrete samples vary within the interval of 11 – 13%. When mixture contains 15% of catalyst waste (K4), greater values of water absorption are obtained.

During research, compressive strength of expanded clay lightweight concrete samples, which have been hardened for 28 days, is determined. Fig. 12 presents average compressive strength values obtained during experimental research.

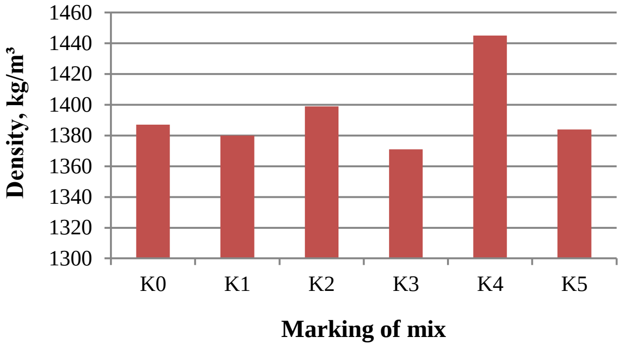

Figure 10. Density values of the expanded clay lightweight concrete samples with catalyst (K1) waste: K0 – without waste; K1 – with 3% of waste; K2 – with 5% of waste; K3 – with 10% of waste; K4 – with 15% of waste; K5 – with 20% of waste

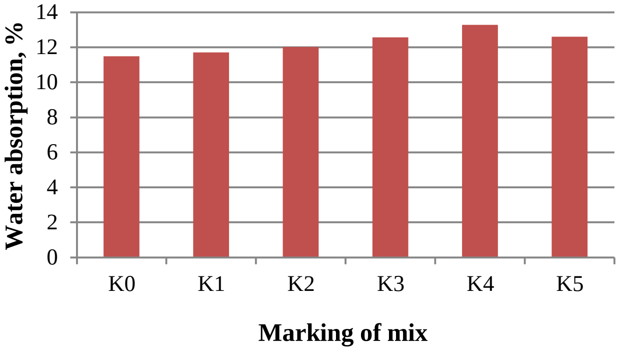

Figure 11. Water absorption values of the expanded clay lightweight concrete samples with catalyst (K1) waste: K0 – without waste; K1 – with 3% of waste; K2 – with 5% of waste; K3 – with 10% of waste; K4 – with 15% of waste; K5 – with 20% of waste

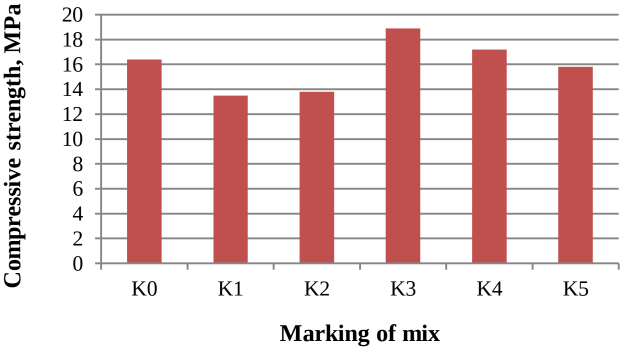

Figure 12. Compressive strength values of the expanded clay lightweight concrete samples with catalyst (K1) waste: K0 – without waste; K1 – with 3% of waste; K2 – with 5% of waste; K3 – with 10% of waste; K4 – with 15% of waste; K5 – with 20% of waste

Results of further research show (Fig. 12) that the compressive strength of samples from control mixture is 16,4 MPa. When part of the cement is replaced with catalyst waste, the average compressive strength values have a wide range: the lowest average compressive strength of samples is 13,5 MPa (mixture K1) and the greatest – 18,9 MPa (mixture K3). The obtained greatest compressive strength values are for samples where 10% (by cement mass) of cement is replaced with catalyst waste. Fig. 12 shows that compressive strength compared to control samples is increased by 15,2% when the mixture contains 10% of waste. The results have shown that compressive strength of 28 days hardened samples with 3% and 5% of replacement of cement with catalyst waste is reduced by, respectively, 26,6% and 25,0% compared to the strength of control samples. The lowest values of such indicators may be determined by the formation of ettringite occurring after 28 days of hardening. The average compressive strength value of samples obtained from mixture K5 is reduced, and the one of the possible explanations is – the reduction of portlandite diffraction peaks. The more cement is replaced with waste, the less of $Ca(OH)_2$ forms after 28 days of hardening.

4. Conclusions

- Technogenic raw material – used catalyst may be utilised in the building ceramics production. About 10% of milled catalyst may be applied to the formation mix, the bigger (20%) amount of catalyst in formation mix has negative influence on the physical-mechanical properties of ceramic body, even burning the ceramic body at the highest burning temperature.
- The results indicate that the additive of milled glass increases density, compressive strength and reserve of porous volume of ceramic samples and decreases water absorption; while the catalyst waste decreases compressive strength, density and increases water absorption. However, applying 10% of each catalyst and glass waste in a formation mix leads to the improved compressive strength, density and reserve of porous volume of ceramic body while water absorption decreases.
- The research of expanded clay lightweight concrete shows that in respect of density and strength, the most appropriate amount of non-milled catalyst waste is 10% (by cement mass). At 10% of catalyst, the average compressive strength of expanded clay lightweight concrete is 18,9 MPa and the average density – 1371 kg/m^3.
- After conducting X-ray diffraction analysis, it is determined that control samples and samples with additive apart from traditional minerals have ettringite, which occurs when 3% and 5% of catalyst waste are used. The existence of non-hydrated alite crystals may be observed when 3%, 5% and 15% of catalyst waste are used, gypsum exists when 15% of the mentioned waste is added.

REFERENCES

1. *Kaminskas, A.* Building Materials. Vilnius, VPU press, 2000: 171 p. (in Lithuanian).

2. *Goberis, S., Štuopys, A*. Registration of Structural Changes in the Refractory Concrete with Waste Catalyst Using Resonance Methods. Materials Science (Medžiagotyra) 2 1996: pp. 40–45.

3. *Szekely, J., Trapaga, G.* Industrial Ecology the Need to Rethink the Materials Cycle: Some Problems, Solutions and Opportunities in the Materials. Journal of Materials Research 10 (9) 1995: pp. 2178–2196.

4. *Youssef, N. F., Abadir, M. F., Shater, M. A. O.* Utilization of Soda Glass (Cullet) in the Manufacturing of Wall and Floor Tiles. Journal of the European Ceramic Society 18 1998: pp. 1721–1727.

5. *John, V. M., Zorban, S. E.* Research and Development Methodology for Recycling Residue as Building Materials: a proposal. Waste Management 21 (3) 2001: pp. 213–219.

6. *Goberis, S., Štuopys, A.* Utilization of Waste Catalyst in Refractory Concrete. Interceram 45 (1) 1996: pp. 16–20.

7. *Goberis, S., Štuopys, A.* Study of Refractory Concrete, with Waste Catalyst Using Refractory and Technical Ceramics 1 1997: pp. 19–22 (in Russian).

8. *Goberis, S., Merlinskaja, I., Pundiene I.* Comparison of Refractory Concrete Produced Applying Waste Characteristics Technical and Technology of Silicate 6 (1–2) 1999: pp. 12–15 pp. (in Russian).

9. *Štuopys, A.* Heat Resistance Concrete Containing Spent Catalyst of Petroleum Refiring Refractories and Industrial Ceramics 38 (1–2) 1997: pp. 23–26.

10. *Hsu, K. C., Tsend, Y. S., Su, N.* Oil Cracking Waste as Active Pozzolanic Material for Superplasticized Motors. Cement and Concrete Research 31 2001: pp. 1815–1820.

11. *Pacewska, B., Bukowska, M., Wilinska, I., Swat, M.* Modification of the Properties of Concrete by a New Pozzolan Waste Catalyst from the Catalytic Process in a Fluidized Bed. Cement and Concrete Research 32 2002: pp. 145–152.

12. *Žurauskienė, R., Petrikaitis, F., Mačiulaitis, R., Špokauskas, A.* Utilization of Catalyst Waste in Production of Sintered Ceramics. Materials Science (Medžiagotyra) 8 (1) 2002: pp. 87–90.

13. *Souza, S., Santos, R. S., Holanda, J. N. F.* Recycling of Petroleum Waste in ceramic Bodies. Materials Science Forum 418 2003, pp. 743–747.

14. *Souza, S., Santos, R.S., Holanda, J. N. F.* Characterization of Petroleum Industry Waste Containing Clayey Masses and Its Application in Structural Ceramics. Ceramics 48 (307) 2002: pp. 115-119.

15. *Souza, S., Holanda, J. N. F.* Densification Behaviour of Petroleum Waste Bearing Clay- Based Ceramic Bodies. Ceramic International 30 2004: pp. 99–104.

16. *Mačiulaitis, R., Vaičiene, M., Žurauskiene, R.* The effect of Concrete Composition and Aggregates Properties on the Performance of Concrete. Journal of Civil Engineering and Management 15 (3) 2009: pp. 317–324.

17. *Paya, J., Monzo, J., Borrachero, M. V., Velazquez, S., Bonilla, M.* Determination of the Pozzolanic Activity of Fluid Catalytic Cracking Residue.

Thermogravimetric Analysis Studies on FC3R-Lime Pastes Cement and Concrete Research 33 (7) 2003: pp. 1085–1091.

18. *Zornoza, E., Garces, P., Monzo, J., Borrachero, V., Paya, J.* Compatibility of Fluid Catalytic Cracking Catalyst Residue (FC3R) with Various Types of Cement. Advances in Cement Research 3 (19) 2007: pp. 117–124.

19. *Su, N., Fang, H.-Y., Chen, Z.-H., Liu, F.-S.* Reuse of Waste Catalysts from Petro-Chemical Industries for Cement Substitution. Cement and Concrete Research 30 (11) 2000: pp. 1773–1783.

20. *Stonys, R., Pundienė, I., Antonovič, V., Goberis, S., Aleknevičius, M.* The Effect of Waste Oil-Cracking Catalyst on the Properties of MCC-Type Castable Materials. Science (Medžiagotyra) 14 (1) 2008: Pp. 59−62.

21. *Aleknevičius, M., Antonovič, V.* Calorimetric Investigations of High Aluminate Cement Hydration in the Presence of Waste Oil-Cracking Catalyst. Cheminė Technologija (Chemical Technology) 2(51) 2009: pp. 33–38.

22. *Souza, G. P., Holanda, J. N. F.* Densification Behavior of Petroleum Waste Bearing Clay-Based Ceramic Bodies. Ceramics International 30 2004: pp. 99–104.

23. *Pinheiro, B. C. A., Holanda, J. N. F.* Processing of Red Ceramics Incorporated with Encapsulated Petroleum Waste Journal of Materials Processing. Technology 209 2009: pp. 5606–5610.

24. *Mačiulaitis, R.; Žurauskienė, R.* Low Porosity Building Ceramics Produced from Local and Technogenic Raw Materials. Vilnius: Technika, 2007: 220 p. (in Lithuanian).

25. *Furimsky, E.* Spent Refinery Catalysts: Environment, Safety and Utilization. Catalysis Today 30(4) 1996: pp. 223–286.

26. *Kizinievič, O., Žurauskienė, R., Špokauskas, A., Mačiulaitis, R.* Application of Catalyst Waste to Ceramics Made of Raw Materials. Materials Science (Medžiagotyra) 11 (1) 2005: pp. 51–56.

27. *Kizinievič, O., Žurauskienė, R., Mačiulaitis, R., Kičaitė, A.* Study of the Technogenic Raw Materials (Catalyst) of the Oil Industry and Possibility to Utilize them in the Constructional Ceramics Production. International Conference “Environmental Engineering“, held on May 22-23, 2008 in Vilnius. Vilnius: Technika, 2008: pp. 175–185.

28. *Tommy, Y. Lo., Tang, W. C., Cui, H. Z.* The Effects of Aggregate Properties on Lighweight Concrete. Building and Environment 42(8) 2007: pp. 3025–3029.

29. *Wu, J.-H., Wu, W.-L., Hsu K.-C.* The Effect of Waste Oil-Cracking Catalyst on the Compressive Strength of Cement Pastes and Mortars. Cement and Concrete Research 33 2003: pp. 245–253.

30. *Malaiškienė, J., Kizinievič V., Mačiulaitis, R., Šemelis, E.* Influence of Assorted Waste on Building Ceramic Properties. Materials Science (Medžiagotyra) 18 (4) 2012: pp. 396–402.

31. Hanawalt Search Manual. Inorganic Phases. Sets 1-48. Pennsylvania, JCPDS, 1998.